HIGH VALENT MANGANESE AS ACTIVATOR OF LUMINESCENCE[1]

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ABSTRACT

In a previous letter (1) it was inferred from the analysis of the emission spectra of Mn-activated zinc orthosilicate and zinc beryllium silicate phosphors, and from the extinction spectra of aqueous solutions of $KMnO_4$ and K_2MnO_4, that the luminescence centers of these phosphors are essentially permanganate and manganate ions, respectively. In addition to this spectroscopic argument it is shown that several properties of various Mn-activated phosphors can be explained from a common point of view with the assumption that their luminescent centers have MnO_4^- or MnO_4^{2-}-like configurations.

Some time ago a series of measurements were made in this laboratory to determine the spectral energy distribution of the luminescence emitted by manganese activated zinc orthosilicate and zinc beryllium silicate phosphors. The results are partly published, partly ready for publication (2, 3). It was found that the spectra of these phosphors can be built up from several bands each of which has the shape of a Gaussian error curve, within the limits of experimental accuracy (about 1% of the maximum luminescence). It was sufficient to assume the existence of four bands having their maxima at 2.35, 2.27, 2.17, and 2.05 eV, or at 525, 544, 567, and 602 mμ. If $I dh\nu$ is the amount of light emitted by photons having an energy between $h\nu$ and $h\nu + dh\nu$, then

$$I(\nu) = \Sigma_k A_k \exp [-B_k (h\nu - h\nu_k)^2]$$

where ν_k represents the band maxima. This is the same formula as that used by M. Lord *et al.* (4), only with different notation. In the zinc orthosilicate phosphor the 2.35 eV green band is predominant, while the spectrum of our zinc beryllium silicate phosphor consists almost entirely of the 2.05 eV red band, the contributions of the other bands being negligible. Similar results were found by K. H. Butler (5) who investigated the emission of a series of zinc silicate and zinc beryllium silicate phosphors. Some of his phosphors show clearly the two extreme types of luminescence, namely, the bands at 2.35 and 2.05 eV, while others have an emission showing intermediate character.

The spectrum of red fluorescing zinc borate, prepared according to Kabakjian (6), is similar to that of zinc beryllium silicate.

It was also found that two compounds of high valent maganese, namely, $KMnO_4$ and K_2MnO_4, can have their extinction curves built up as a superposition of the above mentioned curves. If $E(\nu)$ is the extinction of the solution, then

$$E(\nu) = \Sigma_k a_k \exp [- b_k (h\nu - h\nu_k)^2]$$

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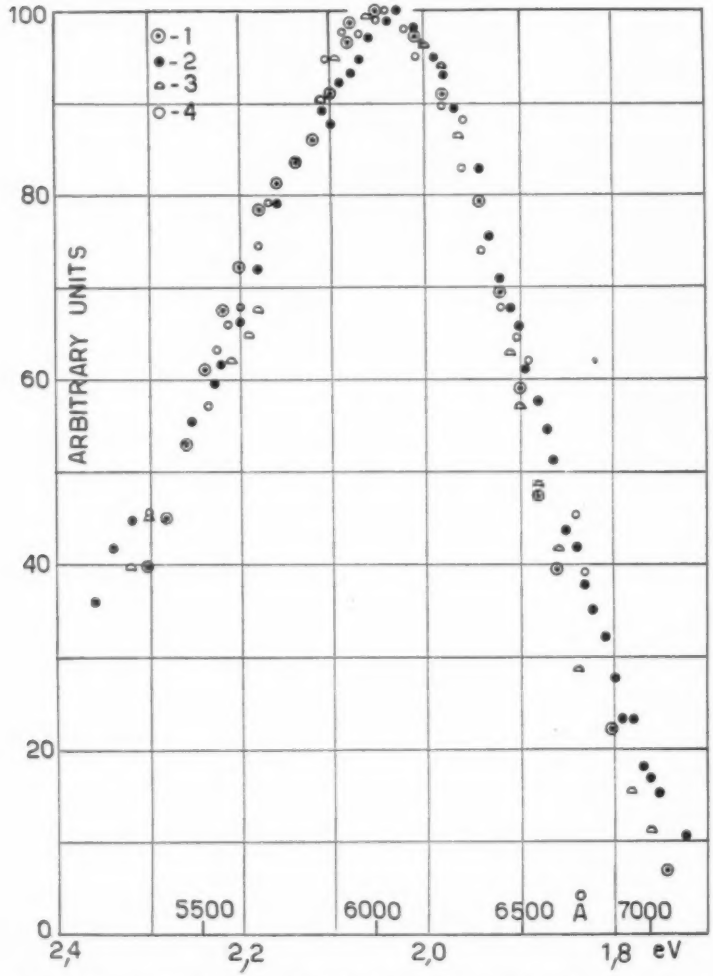

FIG. 1. 1—extinction spectrum of K_2MnO_4 in alkaline solution; 2 and 3—number of emitted quanta (= intensity/$h\nu$) of two samples of fluorescent zinc beryllium silicate made of 15 g. ZnO, 1.0 g. BeO, 10 g. SiO_2, and 1.3 g. $MnCO_3$; 4—number of emitted quanta of fluorescent zinc borate prepared after Kabakjian (6).

The extinction curve of K_2MnO_4 (see Fig. 1) in strong alkaline medium (KOH) consists mainly of the 602 mμ band, while $KMnO_4$ in aqueous solution has bands easily perceptible at 484, 525, 544, 567, and 602 mμ (7). It is to be noted that the absorption maxima of the spectra of perman-

ganates are independent both of the cation and of the solvent used (8). Therefore, the extinction of permanganate solutions has to be attributed to the anion, the valence electron of which is rather protected from outward influence, so that a possible hydration or solvation has no important effect on its energy levels. On the other hand, band width and amplitude of individual bands of MnO_4^- ions may vary with the solvent. Thus we observed on successive measurements that the two principal extinction bands of $KMnO_4$ in pure aqueous solution at 626 and 544 mμ had different relative intensities varying possibly with the CO_2 content of the water, and the bands of the same substance in 1 per cent NaC_2O_3 solution were sharper than in distilled water.

Assuming that the extinction of alkaline K_2MnO_4 solutions is also due to the extinction of the anions, one may conclude from the striking similarity of the spectra that the emission of the zinc beryllium silicate sample is mostly due to centers which contain a manganese atom or an MnO_4 complex, the valence electron of which has the same energy levels as that of the MnO_4^{2-} ion in alkaline solution. The same may be true for the green centers of zinc orthosilicate where we assume that the centers are either MnO_4^- ions or entities like it. In the latter case, the spectrum of the silicate does not coincide with the extinction spectrum of the corresponding solution, only the position of the band maxima is unchanged. The cause of this may be the greater sensitivity of the permanganate ions as mentioned above. There are, in addition, zinc beryllium silicates of various composition as studied by Butler (5), the luminescence of which may be attributed to manganate and permanganate centers existing side by side.

According to previous models, the luminescence centers are generally believed to be positively charged metal ions, yet it is by no means impossible to construct a term scheme in which the centers are negative ions. There is experimental evidence for the existence of such electronegative centers closely related to fluorescence, for example, in complex thallous or stannous halides ($TlCl_4^{3-}$, $SnCl_3^-$, etc.) and in alkali halides (9, 10). Also, it has quite recently been shown by Kroeger and Hellingman (11) that halogen ions play an eminent role in the emission mechanism of zinc sulfide phosphors. It is probable, too, that the fluorescence of tungstates and molybdates is to be attributed to WO_4 and MoO_4 complexes, which are negatively charged anions and, in crystal lattices, are electron acceptors rather than electron donors.

Now, the question arises whether it is possible to determine by direct chemical methods the existence of hexa- or heptavalent manganese in fluorescent substances. This appears to be impossible because of the extremely small concentration of the centers, estimated at 10^{14} to 10^{17} centers/cm.^{3} Kroeger's determination of high valent manganese (12), including valencies from 3 to 7, gives an upper limit of approximately 10^{-5}g. of Mn^{VI} and Mn^{VII} per gram of fluorescent zinc orthosilicate powder. On the other hand, even in translucent aqueous solutions and with colorimetric methods, it is impossible to detect less than 10^{-6} g permanganate. per cm.^{3} in a layer less than 1 cm. thick.

This chemical identification is just as difficult in some other manganese activated phosphors (zinc borate, calcium silicate, calcium carbonate, etc.) which are assumed to contain luminescent centers of similar nature.

This assumption is based on the similarity of their emission spectra. In attempting to determine the minute quantities of high valent manganese in these phosphors, one has to destroy the crystal lattice, as by fusion with Na_2CO_3. During this operation the valency of the manganese may be changed, since fusions of manganese salts with Na_2CO_3 in air produce K_2MnO_4.

There are, however, a few observations related to the chemistry of the centers of several manganese activated phosphors which may be explained from a common point of view by accepting the hypothesis that green and yellow centers are essentially permanganate groups, while orange and red centers contain MnO_4^{2-}-like configurations. The exact position and width of the bands may naturally vary as a function of the matrix. Generally, a well-functioning center is separated from the rest of the lattice so that it behaves much like a gas molecule (13). The greater the interaction between lattice and center, the lower is the fluorescence and the bands are in a more distorted position.

Let us recall at first two properties of manganate and permanganate ions. The former may be oxidized to the latter. The same result is obtained if a green manganate solution, which persists only in strong alkaline medium, is acidified: the liquid changes to the violet color of permanganate, reducing the water to H_2.

The fact that acidification and oxidation produce the same result—a most uncommon feature—may be interpreted as follows. If a strong alkali such as KOH is introduced into a liquid, the K atoms retain their role as electron donors: their valence electrons were already given to the hydroxyl radical (electron acceptor) in the solid and remain there unchanged. If an acid such as HCl is added, the Cl radical will be the electron acceptor, showing that it has higher affinity for electrons than OH. The MnO_4^{2-} ions may also behave as electron donors and split off one of their electrons. However, in alkaline KOH solution they can not do this owing to the presence of a great many other electron donors. In a neutral medium, on the other hand, and as a consequence of particularly fortuitous circumstances, an MnO_4 ion may split off its second valence electron and transfer it to an OH group:

$$2MnO_4^{2-} + 2H_2O = 2MnO_4^{-} + 2OH^{-} + H_2$$

The same may hold in a crystal lattice, for example in Mn activated zinc borate. If the amount of the acid component is increased, the color shifts from orange and yellow to green (14). This may be explained by the assumption that the fluorescing manganate centers turn into permanganate centers due to the enrichment of the matrix with electron acceptors. The same is true with cadmium borates (14): the fluorescence of $2CdO \cdot B_2O_3$ is red and that of $CdO \cdot B_2O_3$ is green.

It was further observed with zinc borate that the fluorescence was green in a product prepared in a current of oxygen, whereas the resulting fluorescence was orange if the fusion took place in a non-oxidizing atmosphere (15). This, too, is compatible with our interpretation of green and red (orange) centers.

As a further example, manganese activated zinc silicate prepared from 1 mol SiO_2 and 1.1 mol ZnO shows a green fluorescence, whereas manganese

activated zinc beryllium silicate made with 1 mol SiO_2, 1.1 mol ZnO, and 0.24 mol BeO is of orange fluorescence. This may be attributed to the enhancement of the basic component. It is known, too, that if a certain part of the ZnO component in zinc orthosilicate is replaced with BeO, the number of red centers increases and that of green centers decreases (5). However, we dare not give an explanation of this latter phenomenon, for we have no data available regarding the greater electron donating ability (basicity) of BeO compared with that of ZnO.

The green and red fluorescence of glasses is well known. In the opinion of Curie (13) the green centers represent a higher oxidized form of manganese than the red centers. That the green and red centers of glasses are identical with those found in zinc orthosilicate or zinc beryllium silicate, for example, is supported by the observation that the luminescence intensity of green fluorescing glasses does not change appreciably in the temperature interval of 20°-200° C., while red fluorescing glasses, on the other hand, are fairly well quenched at 100° C. (16). This phenomenon is also shown by zinc orthosilicate and by zinc beryllium silicate. It was also observed by G. Szigeti and E. Nagy (personal communication) that orange fluorescing zinc beryllium silicate while heated changed its color to green owing to the greater persistence of its green band (see also 17).

Finally, the effect of basicity may also be observed on fluorescing glasses. Linwood and Weyl (16) give a table of fluorescent glasses of various compositions where it may be seen that on enhancing the proportion of the electron donor ingredients the luminescence generally (but not without exception) changes from green through yellow and orange to red. For example, $ZnO \cdot P_2O_5$ shows a yellow, while $Na_2O \cdot ZnO \cdot P_2O_5$ shows an orange fluorescence.

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Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

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THE PREPARATION OF LUMINESCENT SCREENS[1]

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ABSTRACT

The various methods used in the preparation of luminescent screens are discussed and evaluated. The evaluations are made on the basis of the relative importance of such factors as luminescence efficiency, uniformity, thickness, coverage, texture, color, contrast, secondary emisssion, current saturation, and facility of deposition.

INTRODUCTION

Luminescent materials, or "phosphors," are solids which absorb energy and subsequently re-emit it as visible or near visible radiation while maintaining a temperature below that required for incandescence (1). However, since phosphors usually consist of tiny crystals ($\approx 1\mu$) or aggregates of them, it is necessary for most purposes to deposit or spread them out into a layer, coating, or *screen* as it is commonly known.

Some applications for phosphor screens are fluorescent lamps, x-ray fluoroscope and intensifier screens, radioactive luminous markers, dials and indicators, cathode-ray tubes (oscilloscopes, television, radar, flying spot, teleran, "magic eye," image or "snooperscope," electron microscope, etc.), infrared detecting devices, and luminescent signs, markers, advertisements, and decorations.

Each phosphor requires individual treatment and each application has certain requirements to be met by the screen layer. The relative importance of luminescence efficiency, uniformity, thickness, coverage, texture, color, contrast, secondary emission, current saturation, and facility of deposition will determine which method of screening should be employed for a particular device or use.

The various methods of comminution and deposition of phosphors will be discussed with their evaluation. The settling method, comprising sedimentation from (usually) aqueous solutions, will be more fully presented.

COMMINUTION

Most phosphors are synthesized by solid state reactions of finely divided ingredients at high temperatures. The result is usually a lump or cake of irregularly shaped particles. It is necessary to break or comminute it to a convenient or desirable particle size range.

However, solid, inorganic luminescent materials are very sensitive, complicated structures which may be seriously disturbed by chemical attack as well as by mechanical stresses, such as milling, grinding, or crushing. Some types of phosphors, such as the silicates, are more rugged than others, such as the sulfides and fluorides. The silicates, although

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requiring more grinding to break up their hard prarticles, show less loss in efficiency than the sulfides and fluorides. This is shown in Fig. 1 and 2 which indicate the effect of milling time on luminescence efficiency of the two phosphor types.

Compression by a hydraulic press causes a loss of luminescence efficiency[2] in β-ZnS while gradually converting it to α-ZnS as shown in the following table (2):

Luminescence efficiency	*Percent α ZnS*
100	0
50	45
45	56
10.9	90

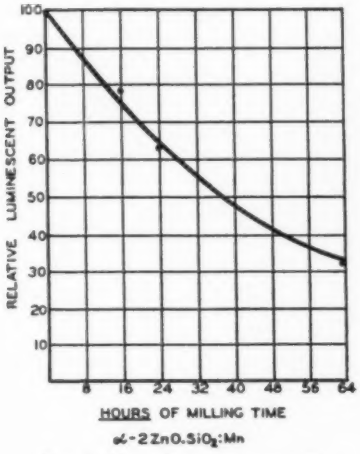

FIG. 1. Data from Leverenz (1)

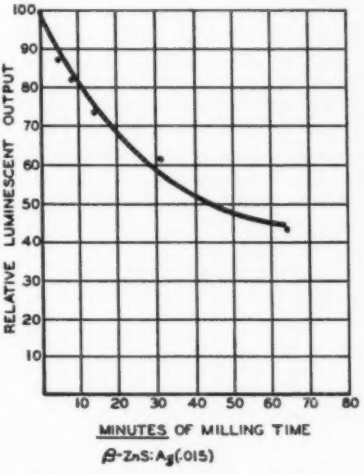

FIG. 2. Data from S. Larach (33)

The ideal case, then, would be a phosphor so synthesized that simple elutriation and stirring would suffice to separate the crystals. For example, many sulfide (selenide) phosphors may be crystallized in such a way as to have a soluble salt (Na_2S, or BaS) as the crystal-crystal bond (3).

Since most phosphors are not constituted as above, some grinding is required. Where a simple mortar and pestle grinding will not suffice, ball milling is widely used. For small batches (<10 g.) a pyrex mill with pyrex slugs is adequate. For larger batches (up to 500 g.) a porcelain mill with flint pebbles or mullite balls is more convenient.

For very careful laboratory work, a quartz rather than pyrex mill is used with quartz balls. This lessens the scorification resulting from abrasion of the pyrex or porcelain by such hard materials as 2 $ZnO \cdot SiO_2$:Mn (4).

[2] The efficiency loss may be due to the "grinding" effect on the dry phosphor particles during compression. Schleede and Gantzkow found a similar conversion of hexagonal ZnS to cubic ZnS with loss in efficiency upon grinding with mortar and pestle (30).

In R.C.A. practice, sulfide-type phosphors are milled less than one hour while such hard phosphors as silicates are given 8 to 16 hours milling in water. Where the phosphor is water sensitive, the powder may be milled in ketones, alcohols, ethers, acetates, or other media which can be easily removed by volatilization.

The milling should be slower for sulfides to prevent incidence of tumbling of balls which may more easily fracture the phosphor crystals. In general, milling should be done at a speed which allows a sliding rather than a tumbling or pounding action on the phosphor particles.

However, even where milling of the phosphor is not indicated from the particle size, it may be advantageous from the point of view of facilitating deposition of the screen.

When solid particles are put in liquid suspension, they usually are enveloped in adsorbed gas or liquid layers of supermolecular thickness which minimize the probability of particle to particle contact (5). In even a short milling, some of this layer may be removed or changed. The mechanical treatment may expose new surfaces, thus spreading the existing layer thinner or otherwise affecting the surface film. The writer has found that better adhesion and cohesion of the screen seems to result when the phosphor suspension is given a few minutes slow milling treatment.

After comminution, segregation of particles is usually accomplished by sieving, elutriation, or differential settling. Although phosphor particles are not spherical in shape, their rates of sedimentation approximate Stokes' law as follows (31, 32).

where V = rate of sedimentation
r = radius of particles in cm.
ρ = density of particles in g./cm.^{3}
ρ_0 = density of fluid in g./cm.^{3}
η = viscosity of fluid in poises (g./cm./sec.)
a = acceleration of gravity

$$V = \frac{r^2(\rho - \rho_0)a}{4.5\eta} \text{ cm./sec.} \qquad (1)$$

A clear-cut separation of particle sizes is virtually impossible; the best that can be expected is a narrow range distribution of particle sizes obtained by repeated fractional separation (6). The procedure is further complicated by the tendency of particles to remain aggregated. Consequently, clusters of small particles are segregated with large particles.

Sieving is only satisfactory for rough separation, or as a safeguard to prevent introduction of large aggregates or foreign particles into the screening suspension. While fine sieves of over 1000 mesh have been made, practical ones such as strong stainless steel sieves are not available in better than 400 mesh and difficult to obtain in finer than 325 mesh. Since the latter can allow particles up to 44 μ in diameter to pass through, they are not adequate for separation of a range of sizes useful in normal screen deposition.

However, it is not too difficult to obtain a reasonable separation by liquid elutriation or sedimentation based on calculations from Stokes' law. (Air elutriation is much more difficult because of the low density of most phosphors and the low viscosity of the gas medium.) Many simple

separators have been devised, such as vertical glass columns with outlets spaced along their length to remove the suspension after fixed time periods. An adequate procedure for most work is to shake the suspension in a Pyrex bottle (e.g., 4 liter) filled to the shoulder, let settle, and reject the deposited particles when all those over the desired range are calculated as having settled. In a similar manner, most of the fine particles can be removed. It is important to thermostat the elutriator or settling container so that thermal convection currents do not offset the gravitational effect considered in Stokes' law.

APPLICATION (DEPOSITION) OF PHOSPHORS

The determination of the method of phosphor deposition depends on such items as: properties of the phosphor; requirements of particular devices; materials, equipment, and time available; economic considerations; and shape or condition of substrate to be coated.

Thus, for example, while a liquid settling method is very suitable for producing a uniformly thick layer on a fairly level substrate, it would be an uneconomical means for applying decorative designs, and too difficult for applying a uniform screen on a cylinder.

The following are brief descriptions of some methods of deposition.

Dusting (air settling).—The substrate is made tacky by application of a binder and the dry phosphor is allowed to fall onto or roll over the surface and adhere. The binder may then be baked out completely.

Kohl (7) employed a variant of this by first depositing sulfur from burning CS_2, shaking the phosphor gently on the sulfur, and then removing the latter by heat.

A more recent practice (3) is to apply a solution of 1 per cent P_2O_5 in acetone containing 0.3 per cent cetyl alcohol (first dissolved in ether). After proper distribution and drying until tacky (interference colors can be seen if the substrate is glass), the dry powder is poured, shaken, or blown onto the binder. After shaking, the excess is removed. Several layers may be built up by baking after each application, and gently repeating the process (Fig. 3).

Other binders can be used, such as alkali silicates, or K_2SO_4 (1 g./500 cc. H_2O). If the screen is deposited on K_2SO_4, it must be retreated with water vapor, redried, and baked. Water vapor alone could be used, with the substrate exposed to it before and after screening (6).

The dusting method is useful for coating substrates of varying curvatures. However, for accurate work (uniform, smooth screens) control of temperature, air currents, and humidity is necessary (drying rate or tackiness of binder is affected) and the phosphor must be free flowing. Furthermore, electrostatic charging affects the deposition process (4) and the screens are not as uniform and tenacious as the liquid settled screen (even with the same binders).

Dry spraying.—This is a variant of dusting. A binder is applied [e.g., 25% solution of K_2SiO_3 or a 10% aqueous solution of $Na_2CO_3 \cdot 10H_2O$ (24)], allowed to dry to tackiness, and a fine spray of dry powder is blown from a gun onto the tacky surface. The screen is then dried and may be air baked (3).

Electrostatic application.—In this method the dry phosphor and the

substrate are oppositely charged so that the phosphor particles are attracted to the substrate. If the substrate is glass, it is heated to the point where it can be uniformly grounded through the heating flame. The dry powder is then charged to several thousand volts by being blown gently past a charged tungsten point or rod. The phosphor deposits on the glass, giving up its charge (22) (Fig. 4).

Electrostatic deposition is especially useful for applying smooth, fine particle coatings on the insides of spherical bulbs or cylindrical or spiral tubings. The dry procedure lessens the effect of dirt contaminants and the problem of coagulation of particles. However, the phosphor must be kept dry and fine in size. The screens show poor contrast in cathode ray tube operation because of the fine particle size (15) and, since no binder is used, have comparatively poor adhesion and cohesion.

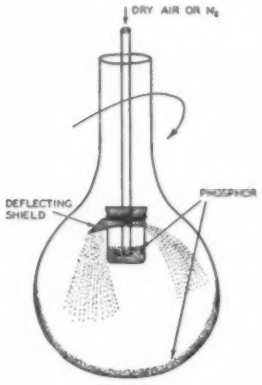

FIG. 3

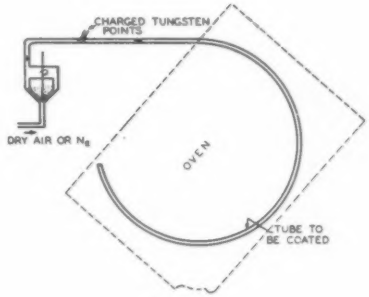

FIG. 4

Wet spraying.—The ground (milled) phosphor is suspended in a volatile medium such as acetone, butyl alcohol, or amyl alcohol, and a binder such as nitrocellulose lacquer is sometimes included. If the phosphor tends to coagulate, a few drops of a deaggregant, such as acetic acid, may be added. The suspension is kept well stirred mechanically or manually while it is being pressure sprayed. Coating of flat surfaces in the open, where the substrate can preferably be rotated, is comparatively simple. However, for coating the inside of cathode ray bulbs where complex air currents result from the closed container, the adjustments have to be determined empirically for each type (a long nozzle extension can be used to bring the spray into the bulb through the neck) (Fig. 5).

The spray is best deposited on a warm substrate to accelerate the volatilization of the liquid medium and lessen the tendency of the "wet" deposit to "run" or slip. After deposition, the screen is air dried, preferably by warm air. The resultant screen can be checked by transmitted light (e.g., lamp and photocell set up which must be calibrated and standardized) to determine whether the desired thickness and uniformity have been obtained. Excess phosphor is trimmed or wiped off the sides where it

is not wanted. In the case of cathode ray tubes which must be vacuum baked, the nitrocellulose binder, if used, must be oxidized by air baking to remove the carbon as CO and CO_2. A temperature of 200°–400° C. with good air circulation is adequate.

The spray technique is advantageous for screen deposition on irregularly shaped substrates (e.g., a cathode ray bulb with small radius of curvature face, or a surface which is partly masked), very large surfaces (e.g., large flat or curved plates), surfaces that cannot be coated easily otherwise (e.g., external surfaces of spheres or vertical wall surfaces).

It is also useful on substrates that might be deleteriously affected by other processes. For example, Nonex glass may excessively weather and show objectionable patterns when screens are applied by liquid settling. The method is fairly rapid once the proper set-up is made.

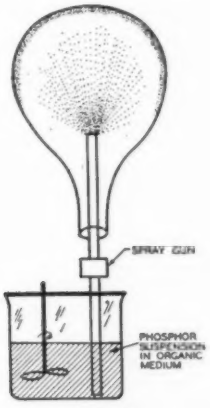

FIG. 5

In spraying, there is usually a large material loss (up to 60% in overspray[3]) and in some cases a time loss (to trim off overspray as in case of side walls of cathode ray bulbs). In cathode ray use, the screens show comparatively poor contrast (15). Actual screen thickness and uniformity are difficult to control. If several phosphors are to be sprayed together, they must be well matched in size, shape, and density to prevent separation on spraying.

"Flow on," "swirling," "flush," or "dip coat" method.[4]—A slurry or thin paste of the phosphor in a binder and diluent is introduced onto the substrate and distributed by flowing or swirling it around the surface until a fairly even coating seems to be obtained. The surface is then inverted and rotated at an angle (Fig. 6) (in the case of a bulb) to allow the excess to drain off and allow the coating to set. The surface is then air dried, usually completely inverted. The excess is trimmed or wiped away and

[3] Overspray is the sprayed material which does not deposit on the substrate area desired coated.

[4] Also called "pouring" in England.

the binder removed by baking out in air. In the case of cylinders (e.g., for fluorescent lamps) the insides are coated by filling with the suspension or slurry and allowing the excess to drain off. The coating is air dried at low (room to 50° C.) temperature and the binder then baked out at higher temperature (e.g., 300° C.). Several coats may be given and the cylinder may be reversed between coatings to obtain greater uniformity (10).

Some sample mixes are:

1. One hundred and fifty grams of willemite with 70 cc. ethyl acetate and 30 cc. of binder (50% ethyl acetate, 50% of 10% nitrocotton in ethyl acetate) are milled 17 hours using 300 g. of pebbles. The slurry is removed by rinsing with a 50-50 mix of ethyl acetate and binder. The mix is diluted with 80 cc. of 1:1 binder in 90 cc. of amyl acetate and 780 cc. of ethyl acetate and strained through a 325 stainless steel mesh when ready to use.

2. Sulfide screens can be made with a solution of 3.5 per cent nitrocellulose in butyl acetate with 5 per cent boric acid in denatured alcohol previously applied to the surface.

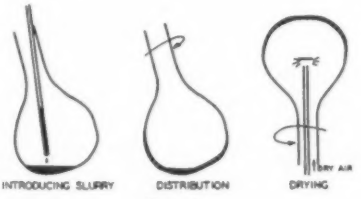

FIG. 6

3. Two hundred and fifty grams of phosphor (i.e., willemite) passing a sieve of 240 BSI mesh is milled 24 hours in 250 ml. of ethyl acetate. Two hundred and fifty ml. of ethyl acetate is then added together with 200 ml. of binder (40 parts of methyl methacrylate such as Diakon D[5] in 100 parts by weight of ethyl acetate). The liquid is shaken for one hour and strained through silk or muslin to remove aggregates. Twenty grams of camphor are then dissolved in the suspension (27). This slurry has the advantage over the nitrocellulose mixes in that there is much less danger of carbonization of the binder due to improper heating.

In applying the paste or slurry, care must be taken to see that no bubbles are admitted with the suspension, or holes may result in the screen. Introducing the suspension close to the surface will help. Should bubbles appear, a hard blow applied to the substrate may break them up.

The flow-on method is useful for wide ranges of particle sizes, shapes, and densities, is fairly rapid, and can be used for coating substrates of varying curvatures. There is some loss, usually in overflow; exact thickness is difficult to achieve; dirt specks or very large particles tend to be centers of irregular flow; and air currents, humidity, and temperature must be carefully taken into account in carrying out the process.

Evaporation.—In this process, the material to be applied is heated in a

[5] Trade name.

vacuum to a temperature sufficient to evaporate the desired amount of material, which deposits on the cooler surface of the substrate.

The method has proven unsatisfactory for phosphors because of a loss of luminescence efficiency by evaporation. Attempts to deposit sulfide screens by evaporation technique gave layers of low efficiency (11) as did zinc oxide and zinc fluoride (12).

Evaporated screens have been successfully used on dark trace tubes (e.g., 4AP10) where the screen consists of potassium chloride. In the case of the 4AP10, the evaporator cup is positioned about 70° from the normal to the face of the bulb and affixed to the cone wall (via bead) about 2 in. from the face (Fig. 7). After the envelope is exhausted, the salt is evaporated by high frequency application to the metal cup. The process takes but a few minutes and a good uniform screen can be obtained.

Synthesis on evaporation.—A variant of the above process is the actual synthesis of the phosphor screen during evaporation (or sublimation).

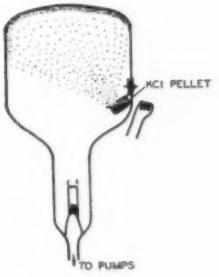

FIG. 7

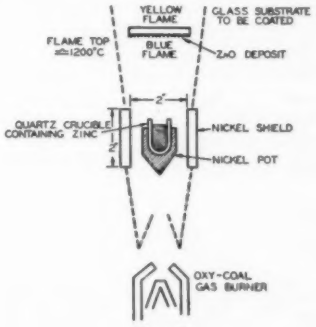

FIG. 8

Some ZnO screens have been prepared by heating zinc in a quartz crucible in the reducing part of the flame (Fig. 8) (13). It is reported (34) that fairly efficient fine-textured screens may be deposited by this method.

Electrophoresis.—In this method, the phosphor in liquid suspension is attracted to an immersed electrode upon which it deposits.

At the interface between two phases there exists an electric charge. In the case of a solid-liquid system, an externally applied potential difference causes a movement of the particles of disperse systems.

Phosphor particles in suspension can be made to migrate in an electric field and will deposit on the electrode of opposite charge (actually, the particles are led to the liquid layer next to the electrode where they are altered electrolytically, coagulated, and deposited). Smooth, fairly pore-free deposits are made because, unlike metal electrodeposition, the particles are non-conductive. Hence, they cease to conduct currents of any appreciable intensity as soon as the deposit reaches a minimum thickness. This automatically displaces the current toward the part of the surface which is not yet well coated (18).

Except for purposes of measurement of phosphor surface charges,

there is not much advantage to this method. It is uneconomical merely to apply screens in this manner, since screens of as good a quality can more easily be deposited by other means. The control necessary on particle size, e.m.f., current, suspension composition, temperature, etc., and the need for a conductive substrate further militates against its use.

Painting.—One of the simplest and most rapid methods of depositing a phosphor layer is to paint a slurry or paste suspended in a volatile medium onto the substrate with a brush or other applicator (e.g., doctor's knife). Such a mixture can be made by stirring the powder with amyl or ethyl acetate or other volatile material. A nitrocellulose binder can be added, if greater adhesion is needed. If the sample is to be vacuum baked, it is necessary in the latter case to oxidize the nitrocotton to prevent carbonization. Isobutyl methacrylate can be substituted for nitrocellulose if no air bake is advisable before vacuum bake since it does not require oxidation before volatilization. For even greater adhesion and abrasion resistance as well, an aqueous slurry containing potassium or sodium silicate binder is recommended. Care must be taken to dry the silicated layer slowly to prevent flaking.

For a real paint (pigment, vehicle, and diluent) where subsequent high baking is not required (i.e., not for vacuum tubes), the following mixture works well.

Stock solution	*Paint mix*
Polystyrene XMS-10,023 or equivalent—61.7 lb.	Stock solution—500 cc.
Toluol—8 gal.	Xylol—250 cc.
Xylol—8 gal.	10% Aluminum stearate in toluol—37.5 cc.
Butyl acetate—8 gal.	$CaBO_4$—17 g.
Dibutyl phthalate—2 gal.	Luminescent SrS < 150 mesh—340 g.

If alkaline earth phosphors are to be used (CaS, SrS), special precautions must be taken to use a vehicle of low acid number (to prevent hydrolysis and decomposition) and of sufficient covering power to prevent penetration of moisture.

For best results on opaque surfaces, a luminescent paint is applied on a white background or undercoat to allow for maximum reflection of light which would otherwise be absorbed in the substrate. However, it is important to use materials in this undercoat which will not tend to poison the phosphor (e.g., lead).

Printing.—Phosphor layers can be applied by most of the standard printing methods such as printing press, lithography, silk screening, and decalcomania.

Silk screening.—This process is essentially one where paints or other printing media are forced through the openings in a silk (or organdy or metal) cloth and deposited on the printing surface. If a design or pattern is desired, a stencil can be first applied to the cloth so that the printed pattern will be a facsimile of that on the cloth. The thickness of the deposit can be roughly controlled by the set space between cloth screen and substrate. As a rule, the finer the detail to be printed, the finer the cloth required (14). However, the consistency of the paint or paste also determines the mesh cloth which can be used and vice versa.

In practice, after the silk screen is prepared, (e.g., with stencil), a paste

of the luminescent material (a formula similar to that given in the section on painting is satisfactory) is put on the screen and pushed through the mesh openings with a rubber squeegee. The silk screen is lifted off and the coated object is air dried.

The process is very useful for rapid coating of such diverse materials as paper, cardboard, cloth, glass, plastic, wood, etc.

Decalcomania.—A phosphor pigment can be incorporated in a decalcomania transfer paper by printing or silk screening the paste onto the glue sized paper. The decal can be made either positive or negative (depending on method of affixing desired) and can have a metallic film or pattern backing (by first applying a metal leaf or layer to the paper before the phosphor is applied). Designs, patterns, etc. can be made on the decal as in the case of other printing media.

The decal is a handy method of rapidly applying a phosphor layer, pattern, or design.

However, as in silk screening, uniformity of thickness ($\pm 10\%$) is difficult to achieve, and the decal cannot be affixed to a doubly curved surface. Present formulations do not give a layer that can be vacuum baked (e.g., in CR tubes).

Other printing processes.—Besides the silk-screen and decalcomania methods of phosphor printing, luminescent materials can also be applied by letter press and lithography (25). Care must be taken here as well in keeping out deleterious reagents (i.e., high acid number resins in case of sulfides) and not applying such pressure as would deaden the phosphor crystals.

Molding.—Phosphor powder can be mixed with plastic molding powder and injection or compression molded to form sheets or other subjects. The plastic itself should be non-absorbing in the visible region to allow light transmission to and from the phosphor. The advantages are that a luminescent layer is obtained which has most of the advantages of the plastic [resistance to handling, can be drilled sawed, bent (if thermoplastic) etc.] and, if not too thick, can be irradiated and excited from any angle.

As in the case of painting and silk screening, care should be taken in the above formulation, to exclude moisture or high acid number ingredients especially if alkaline earth sulfide phosphors are to be used.

Imbedding.—If a screen is desired imbedded on the surface of a plastic, the phosphor can be deposited in a medium which will dissolve the surface layer of the plastic. After the phosphor is deposited, evaporation of the medium (e.g., acetone) will leave a thin layer of the plastic over the phosphor. If uniformity of phosphor screen is not critical, it can be molded so as to appear on only one surface (see molding).

Phosphors may also be imbedded in glass or enamels so that the surface maintains the resistance of glass to solvents, contaminants, and abrasion (19, 20, 21).

Chalk.—A convenient method of depositing a layer of phosphor particles is to write or mark such a layer using a piece of chalk with a phosphor component. The method is ideal for temporary illustrations, signs, markings, or backgrounds, and the chalk is not too difficult to prepare. It can be simply made by mixing calcium sulfate hemi-hydrate with the

phosphor, mixing with water, and letting set in a mold (26). (A convenient mold can be made by wrapping heavy wax paper around a dowel stick, inserting in sand, and removing dowel stick. The plaster does not adhere to the paper.)

Uniform screens cannot be made from chalk and if permanency is desired, the deposit would have to be coated with a lacquer or other transparent film. However, this method is advantageous in that it can be applied wherever ordinary chalk can be applied and is of course a very rapid means of affixing phosphors to a surface.

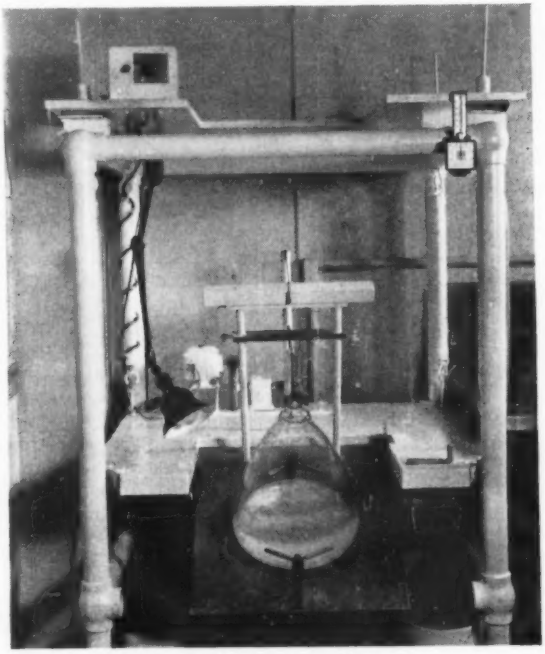

FIG. 9. Laboratory pouring device

Liquid settling.—This method consists of applying a liquid (usually an aqueous suspension of the phosphor) onto the substrate, allowing the phosphor to settle out, then removing by decantation (Fig. 9), siphoning or evaporation, the supernatant liquid from the deposited screen.

The method is very important for use in television and other cathode ray tube fabrication as well as for studying the characteristics of the screens themselves. This is due to the settled screen's controllable thickness, uniformity, and texture, its reproducibility, and material economy (all the phosphor goes into the screen itself).

The light output of high voltage cathode ray tube screens (as measured on the side away from the electron beam) will vary with screen thickness

(Fig. 10) (29). This is due to increased penetration of the electron beam with increase in voltage, absorption of the light in the screen, and the changes in the secondary emission of the screen brought about especially by variation in the amount of glass exposed under the material.

Consequently, cathode ray tubes (especially high voltage) are usually made with optimum thickness screens for any particular operating voltage. Thus a control of screen thickness and uniformity is not only necessary from the practical standpoint of making efficient tubes, but from an experimental one as well, of measuring the characteristics of the screen itself.

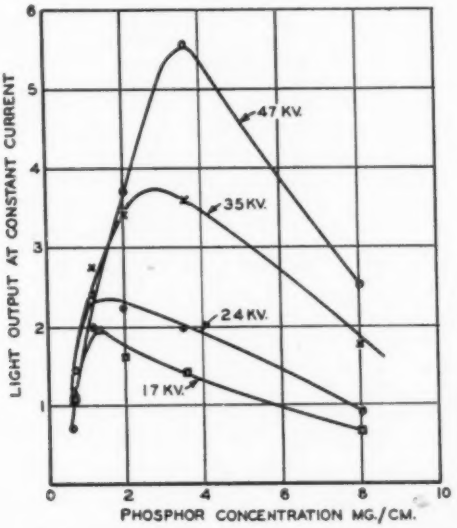

FIG. 10. Curves showing the effect of screen thickness on light output from a reflective aluminum-backed blue zinc sulfide phosphor under electron excitation. (Reproduced by permission from "Preparation and Characteristics of Solid Luminescent Materials." Edited by G. R. Fonda and F. Seitz, published by John Wiley & Sons, Inc., 1948.)

There are numerous procedures for applying screens by liquid settling. In general, they may be classed as follows:

1. No binder or electrolyte added to the suspension
2. Binder only added to the suspension
3. Electrolyte(s) only added to the suspension
4. Electroylte(s) and binder added to the suspension

In the first case, adhesion is very poor and aggregation may be excessive. [The tendency for particles to aggregate is ever present, presumably due to short range forces (both permanent and induced dipole attractions) and to longer range London's forces (wave-mechanical attracting forces due to mutual electron disturbances). Apart from the particle-particle interactions there are complex forces due to the adsorbed films on each particle.]

Liquid settling without added agents is mainly used to study the screen characteristics where the presence of foreign ions, etc., might affect the result. It is also useful to check the latter effect, especially where the electrolyte or binder is suspected of having or being a "contaminant."

Several methods employing binders but no electrolytes have been used. In one, the substrate is first treated with a layer of gelatine and dried. The phosphor suspension is then introduced onto the gelatine and the phosphor allowed to settle out. The liquid is then removed and the screen dried (16). Coagulation usually takes place, however, unless an agent such as acetic acid is added.

Another procedure is to suspend the phosphor in an organic medium such as acetone and add nitrocellulose as the binding agent. If a vacuum bake step is to follow (e.g., cathode ray tubes) an air bake must first be performed to prevent carbonization of the nitrocotton.

Where the screens are comparatively thin (about 2 mg./cm.^{2} or less) and need not withstand rough treatment [e.g., rewetting, and organic film application (9)], electrolytes alone are sufficient to prevent agglomeration and slippage and allow uniform, smooth-textured screens.

Various electrolytes have been found helpful in lessening the tendency of the particles of building up a surface layer which prevents or decreases the adhesion of the phosphor to the substrate. High mobility hydrogen ions can be provided by introducing ammonium carbonate ($NH_4\ HCO_3 \cdot NH_4NH_2CO_2$) which will help discharge negatively charged phosphor particles. The slightly alkaline solution of ammonium carbonate may also serve to lessen the inactive layers on the phosphor particles (weak acids may also aid in this), and aids in producing an active surface which will readily react with the siliceous surface of the glass substrate (4).

Other electrolytes successfully used are acetic acid, lithium hydroxide, sodium sulfate (or mixtures of them), ammonium halides, and ammonium hydroxide.

For thicker screens (up to the 20 mg./cm.^{2} range) or for strongly cohesive and adhesive screens [e.g., for aluminizing which requires deposition of an organic film on the screen (9)], a binder usually is necessary. If the screen is to receive a vacuum bake and still retain its cohension and adhesion, a silicate binder such as potassium, sodium, or ethyl silicate is indicated. These not only tightly bind the phosphor to the substrate, but permit rinsing or rewetting of the screen without washing it off. In the case of the alkali silicates, there is some ionization which may affect the surface of the particles in a manner similar to the electrolytes described above.

However, it is also useful to add an electrolyte to accelerate the gelling of the silicate binder. An inorganic salt such as potassium aluminum sulfate, zinc sulfate, or an hydroxide (17) will hasten the gelling of the silicate and shorten the time necessary to remove the supernatant liquid.

For example, experiments performed by Hazel and Stericker (28) indicate the effect of the addition of sodium sulfate to potassium silicate (Kasil #1).

Samples 1, 2, and 3 remained clear for a period of 4 days. Sample 4 was clear at first but became somewhat turbid after 4 days. Sample 5 was slightly milky after 24 hours and very milky after 48 hours. After 72 hours it gelled on the bottom of the glass.

Sample No.	ml. of solution containing 10% Kasil #1 (approx. 0.49% K_2O, 1.23% SiO_2)	ml. of M/2 Na_2SO_4 solution	ml. of H_2O
1	100	0	60
2	100	5	55
3	100	20	40
4	100	40	20
5	100	60	0

When a sulfide phosphor was settled in the above solutions, adhesion of the screen to the glass increased with increasing concentration of Na_2SO_4.

In the use of silicate binders, it is important to dry the screen slowly. If dried too rapidly, a fairly impervious layer of silicate forms on the screen surface. As further drying and/or baking is followed, the entrapped moisture tries to push through. The force is strong enough to lift the screen from the substrate. The screen may then flake off easily. Drying is best done by using dry, room temperature air with no heat applied to the screen.

Alkali silicates hold a high percentage of water. If a cathode-ray tube is pumped without prior baking of the silicated screen, the evacuation process may be long and difficult before high vacuum is obtained. If the screen is first air baked, there is sufficient breaking down of the silicate to release the excess water and evacuation can then proceed more easily. In the case where further processing of the screen is to be done, such as organic filming or aluminizing, the screen should be baked in air first to obtain a rugged, tight layer that will withstand wetting and organic film application. Infrared lamp baking may be substituted for oven baking.

As mentioned before, there are numerous variations which have been used in settling screens. These include use of ultraviolet irradiation during settling, addition of inert fine particle ZnCdS as a "sticker," addition of copper salts (3), albumen (16), etc.

For most purposes an alkali silicate binder added to the settling suspension is preferred.

In a typical case, a screen for use at 30 kv. in the electron microscope may be deposited as follows:

Clean all glassware thoroughly. Hot chromic acid followed by distilled water rinses is effective. Set the glass plate in a deep container such as a battery jar or crystallizing dish which in turn is set on a cork ring or other surface fairly free of vibrations. Mill the phosphor (e.g., ZnCdS such as RCA 33-Z-605B) 20 minutes in double distilled water and pour into a Pyrex glass-stoppered bottle. Measure the area of the bottom of the dish (e.g., 200 cm.^{2}). For 30 kv. operation, 6 mg./cm.^{2} has been found best in these laboratories. Hence, a total of 1200 mg. of phosphor would be needed. Measure out sufficient suspension to give 1200 mg. of phosphor, into an Erlenmeyer flask. Dilute to 200 cc. with double distilled water and add approximately 8 cc. of 25 per cent potassium silicate,[6] and approx. 20 cc. of 1*N* Na_2SO_4. Cover the substrate with about 2 in. of double distilled water to which has been added 25 per cent potassium silicate (40 cc./l.) and 1*N* Na_2SO_4 (100 cc./l.). Pour the well-shaken suspension onto the water "cushion" and allow to set one hour. Siphon off the water slowly, dry the screen, and bake it at 350° C. for 5 minutes.

[6] Supplied as "Kasil #1" by Philadelphia Quartz Company, Philadelphia, Pa.

In the case of cathode ray bulbs, the screens can be deposited sufficiently tightly so that the supernatant liquid can be decanted off rather than siphoned. A vibrationless "tilting" platform is useful in carrying out this process (see Fig. 9).

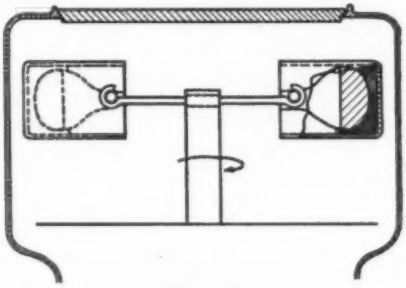

FIG. 11

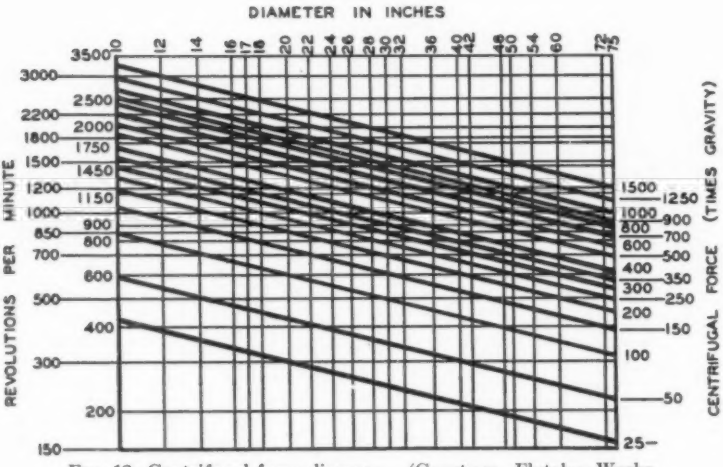

FIG. 12. Centrifugal force diagram. (Courtesy—Fletcher Works, Philadelphia, Pa.)

As has been pointed out, the settling process is advantageous in depositing uniform, reproducible, economical, wide particle size range screens of required thicknesses.

However, all the ingredients and apparatus must be kept very clean because the phosphor is more easily contaminated in the wet state. The process is slower and requires more space than many others. Control of temperature is necessary because of its effect on electrolytes, binders, and convection currents which affect screen uniformity.

Centrifuge.—This method is a special case of the liquid settling process. The gravitational force in the usual settling process is here greatly enhanced by centrifugal force, resulting in a more adhesive, more tightly packed screen layer but one which otherwise has the same properties and

characteristics (i.e. efficiency, contrast, etc.) as does the regular (gravitationally) settled screen.

The process consists of setting the substrate [bulb, plate (held in container), etc.] in the cups of a centrifuge (arm and bucket type), adding suspension as in the regular settling method, and centrifuging for two to

	Method of Deposition									
	Air settling	Liquid settling	Centrifuging	Wet spraying	Flow coating	Painting	Printing	Electrostatic	Molding, imbedding	Chalk
Screen Qualities Desired										
Screen uniformity	5	1	1	2	4	8	7	3	6	9
Screen contrast*	2	1	1	4	3	—	—	5	—	—
Accuracy of screen weight and thickness	3	1	1	2	4	7	5	6	5	8
Cohesion and adhesion	6	4	3	7	5	2	8	10	1	9
Rapidity of deposition	8	9	5	6	7	2	3	4	10	1
Materials and Equipment Available										
Small radius of curvature or irregularly shaped substrate	7	9	8	6	5	2	10	4	3	1
Very large phosphor particles (approx. 20 μ)	4	8	7	9	6	3	5	10	2	1
Very small phosphor particles (approx. 1 μ)	9	10	2	7	8	4	5	3	6	1
Minimum control of temp., air currents, humidity	8	7	4	6	9	2	3	10	5	1

* As measured under similar conditions when excited by cathode rays.

Fig. 13. Each of the various deposition methods have advantages for particular applications and conditions. The above chart gives a rough comparison of the important methods in terms of some applications and conditions. (# 1 is best, # 10 is worst.)

five minutes depending on height of liquid, adhesion necessary, etc. (Fig. 11). The buckets or cups must be well balanced and the centrifuge operated so as to give a minimum of vibration so that the deposited screen will not be disturbed. . Obviously, the substrate should be normal to the centrifugal force if even, uniform deposits are required. The screened substrate can then be removed from the cups after coming to rest and the supernatant liquid removed as in liquid settling. Usually, the screen is sufficiently adherent so that the liquid can be poured off by hand without the screen being disturbed.

The ratio of forces exerted in the process of packing the screen material centrifugally and by normal gravitational method is indicated by the equation (8):

$$\frac{F_c}{F_n} = \frac{4\pi^2 rn^2}{g} \tag{2}$$

where Fc = centrifugal force
Fg = gravitational force
r = radius of rotation
n = speed of rotation
g = acceleration by gravity

The relation between speed of revolution, size of centrifuge and centrifugal force is shown graphically in Fig. 12.

The centrifugal method is indicated and effective where very small particles are to be deposited, where the settling medium is viscous, and where gels may form in the normal settling time. Precautions must be taken to assure matching of loads on the centrifuge arms to prevent vibrations, and proper shielding is necessary as a safety measure.

ACKNOWLEDGMENT

The writer wishes to thank H. W. Leverenz, D. W. Epstein, F. H. Nicoll, S. Larach, and L. Pensak for their many helpful comments.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

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ELECTROSEPARATION OF TRACES OF SILVER FROM PALLADIUM[1]

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ABSTRACT

A study was made of the electroseparation of silver and palladium using several complexing agents. Cyanide was found to produce the most favorable separation while, at the same time, allowing a nearly complete recovery of silver. It has been shown that repeated electrolyses are feasible, and that, by such means, silver, of high specific activity and chemically and radiochemically free from palladium, can be separated from the palladium from which it is produced by neutron bombardment.

INTRODUCTION

Certain studies in this laboratory required the use of radioactive silver of high specific activity. The most satisfactory method for producing such silver appeared to be by neutron bombardment of palladium. Most precipitation methods for the recovery of a tracer require the addition of a "carrier," resulting either in a decrease of specific activity or in a more cumbersome procedure if the carrier is not an isotopic one. Electrolytic separation without the addition of "carrier" looked promising, but much of the required information about deposition potentials was found to be lacking. A polarograph was employed to obtain the necessary data.

When two or more elements can be electrodeposited from a given solution, it is sometimes possible to separate one element from the other by electrolysis with a carefully selected and well regulated potential. The selection of a suitable potential can be made on the basis of electrolytic information obtained polarographically (12). Regulation of the potential has been carried out manually and, in a technique popularized by Sand (18) and called "internal electrolysis," by chemical dissolution of the anode. In recent years, instruments have been designed for regulating electrode potentials automatically (3, 4, 6, 7, 11, 13, 16).

Studies involving the electroseparation of a trace usually require special consideration in order to minimize losses from adsorption and coprecipitation during a separation, and from dissolution of the deposit during the washing process. The separation discussed below was favorable in that a trace element, silver, was deposited and a macro constituent, palladium, was left behind in solution. Furthermore, the separation concerned the deposition of silver, a process about which much information was available.

Suitable silver and palladium traces were prepared simultaneously by bombarding a sample of natural palladium with neutrons. By exercising

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care in the selection of the age of the bombarded sample, it was possible to work with a mixture of a pure silver activity and a pure palladium activity. The chains of primary interest were:

$$Pd^{110}\ (n, \gamma)\ Pd^{111} \xrightarrow[26\ min.]{\beta^-} Ag^{111} \xrightarrow[7.5\ d.]{\beta^-} Cd^{111}\ (stable) \qquad (1)$$

$$Pd^{108}\ (n, \gamma)\ Pd^{109} \xrightarrow[13\ hr.]{\beta^-} Ag^{109}\ (stable). \qquad (2)$$

The first chain was important because it was the source of the silver tracer; the second, because it was the source of the useful palladium tracer and, at the same time, more than 95 per cent of the silver produced in the sample. The production of such a large amount of stable silver compared to radioactive silver was unimportant only because the total amount of silver produced was apparently negligible (less than 1%) compared to the amount of silver introduced as an impurity in the various reagents.

The fact that both Ag^{111} and Pd^{109} emit only β particles of nearly the same energy was a serious disadvantage. In order to analyze a mixture of these activities, it was necessary to prepare a decay curve or to make a radiochemical separation. The former was used in the present study.

EXPERIMENTAL DETAILS

Apparatus

Polarograms of reactions at a stationary platinum electrode were recorded automatically by a modified (20) Sargent Model XX Polarograph. The modifications were similar to those later incorporated in the Model XXI. A potentiometer was used to check the initial and final voltages of each polarogram. The solutions were maintained at 25° ± 0.1°C. by means of a thermostated bath.

All pH measurements were made with a Beckman Model G Meter equipped with a glass electrode having a small correction for sodium ion. The electrode was calibrated with a standard buffer solution before each use.

The electrolytic cells were of the type shown in Fig. 1. The design was essentially that used by other workers (1, 2, 14) with the following modifications introduced by Ehrlinger (5): (a) a "scotch tape" gasket between the glass cylinder and the platinum electrode, and (b) agar salt bridges to allow the anode and the reference electrode to be placed outside the solution. The use of a fresh set of salt bridges for each determination was facilitated by making each bridge in two sections which were connected by ball and socket joints (not shown in Fig. 1).

The potential on the cathode was controlled within ±3 mv. (often within less than ±1 mv. during a fifteen hour period) by using a regulator designed at our laboratory (11, 16). The current that passed through the reference electrode, a saturated calomel electrode of about 50 $cm.^2$ area, was 2×10^{-8} amp./mv. unbalance. The capacity of the anode-cathode circuit was 1.0 amp.

All radioactive samples were counted by means of a thin mica end-

window Geiger-Mueller counter tube contained in a standard aluminum-lined lead housing. The samples were maintained at a predetermined distance from the window by an aluminum support.

Preparation of solutions

All chemicals used in this study were reagent grade. All solutions were prepared with distilled water.

The radiation characteristics of Pd^{109} and Ag^{111} tracers corresponded to those reported in the literature (15). The yield of Pd^{109} was checked by adding a small amount of natural silver (as nitrate) to an aliquot of a solution of bombarded palladium, precipitating silver chloride, and counting the palladium remaining in solution. The yield of Ag^{111} was determined in another aliquot by allowing the palladium activity to decay to a negligible value and then counting the silver.

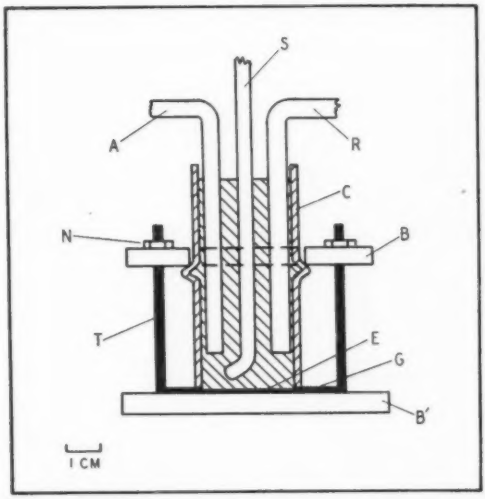

FIG. 1. Electrolysis cell. A, anode bridge; B, brass collar; B^1, brass base; C, glass cylinder; E, electrode; G, gasket; N, brass nut; R, bridge to reference electrode; S, stirrer; T, threaded brass bolt.

Polarographic solutions contained 1.00×10^{-3} M reducible ion and 0.1 M or more complexing agents as background electrolyte. The silver solutions were prepared from weighed amounts of silver nitrate. Palladium solutions were prepared by dissolving a known amount of the metal in a mixture of hot sulfuric and nitric acids. After the bulk of the nitrate ion had been removed by fuming, the excess acid was neutralized by adding a solution of sodium hydroxide until a permanent precipitate appeared. Sufficient background electrolyte was then added so that, after dilution in a volumetric flask, the solution contained a known concentration of complexing agent plus an indefinite amount of sodium sulfate. The

concentration of complexing agent was 0.1 M with two exceptions: (a) in the thiocyanate solution, where it was necessary to have a 0.3 M background to prevent the slow precipitation of silver, and (b) in certain cyanide solutions, where the hydrogen wave, which followed the silver wave very closely, was shifted to more negative potentials by adding sodium hydroxide.

All solutions for electrolytic studies were prepared in exactly the same way as those just described for the polarography of palladium except that neutron-bombarded palladium was employed. The concentration of the background electrolyte and the palladium were the same as before but the

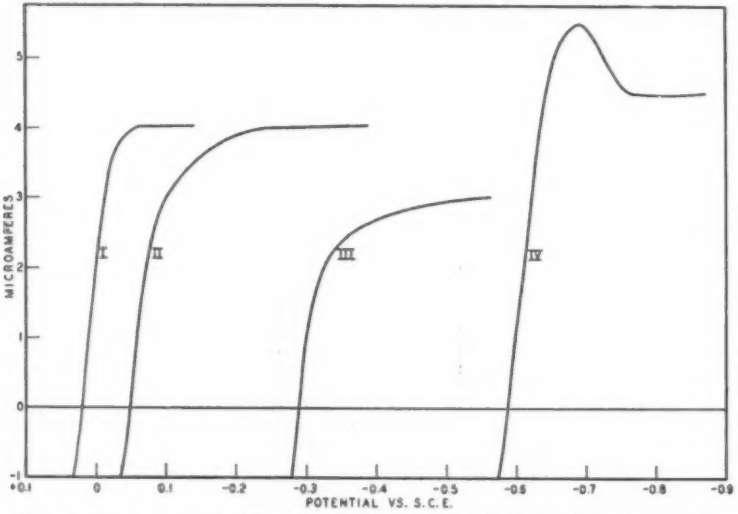

FIG. 2. Polarograms of millimolar silver complexes obtained with a dropping mercury electrode using automatic recording. I, 0.1 M NH_4OH; II, 0.3 M KCNS; III, 0.1 M $Na_2S_2O_3$; IV, 0.1 M NaCN.

solutions contained, in addition, about 10^{-9} M silver exlusive of the amount introduced as an impurity. Table I shows the concentration relationships that were measured for the bombardment conditions employed in this investigation.

General procedures

Polarography.—Reduction waves were obtained for 30 ml. portions of solutions in the usual way using dropping mercury and stationary platinum electrodes (17, 19). All solutions were de-aerated by bubbling oxygen-free nitrogen through the solution before a polarogram was begun. During the course of the polarization an atmosphere of nitrogen was maintained above the solution.

The polarograph was also employed to test the reversibility of reactions by changing the direction of polarization, i.e., proceding from negative to

positive potentials. Whenever a regular polarographic solution was examined in this way, a reversible reaction produced a dissolution wave which was an extension of the reduction wave. When the reaction was irreversible, the dissolution wave was displaced to a more positive potential so that it was no longer an extension of the reduction wave. Dissolution behavior of deposits was also studied by employing an electrode recently plated with silver or palladium and a solution containing only a background electrolyte. As shown in Fig. 3 and 4, this empirical procedure produced results from which one could estimate the ready reversibility or irreversibility of a reaction. The method was used to study reactions in palladium

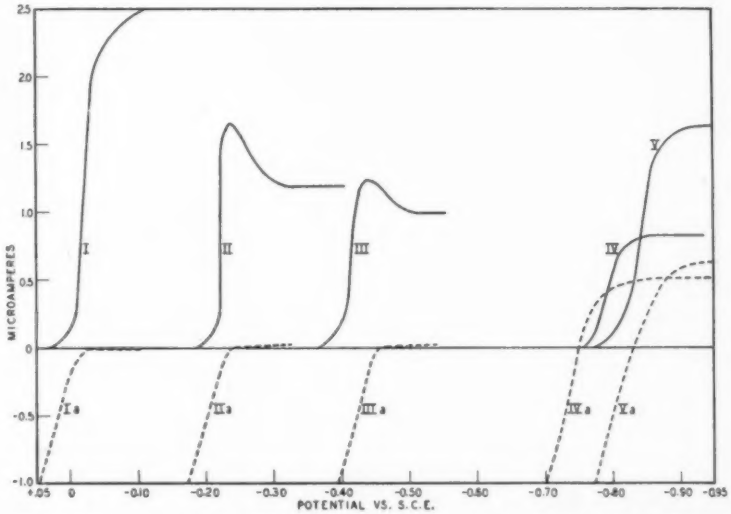

FIG. 3. Polarograms of millimolar silver complexes obtained with a stationary platinum electrode using automatic recording. I, 0.1 M NH_4OH; II, 0.3 M KCNS; III, 0.1 M $Na_2S_2O_3$; IV, 0.1 M NaCN + 1.0 M NaOH; V, 0.1 M NaCN. The "a" curves are the corresponding dissolution waves.

solutions where irreversible reduction waves did not precede hydrogen discharge.

Electrolysis.—A 20 ml. portion of solution was electrolyzed with stirring for a fixed length of time. Then, without breaking the electrical contact, a large part of the solution was removed by suction and the remainder displaced by flushing the cell with about 200 ml. of a salt solution such as 0.1 M sodium chloride, perchlorate, nitrate, or sulfate. Finally, after washing the cell with 100 ml. of distilled water, electrical contact was broken and the cathode removed, dried under an infrared lamp, and counted.

At the completion of a determination, the cathodes were cleaned by boiling in concentrated nitric acid; this removed the scotch tape as well as a large part of the active silver. In order to remove the remainder of the activity, it was necessary to allow the electrodes to stand in a concentrated

solution of sodium cyanide. After removal from the cyanide, the electrodes were washed thoroughly with distilled water, dried under an infrared lamp, and checked with a counter. It was usually necessary to allow the electrodes to remain in the cyanide for an hour or more to reduce the activity on the electrode to "background" level.

Counting.—The procedure used in the radiochemical analyses was the same as that described by Hume, Ballou, and Glendenin (8). Liquid samples were analyzed by evaporating an aliquot of the sample, usually 0.100 ml., on a 1 in. watch glass. At the completion of the evaporation,

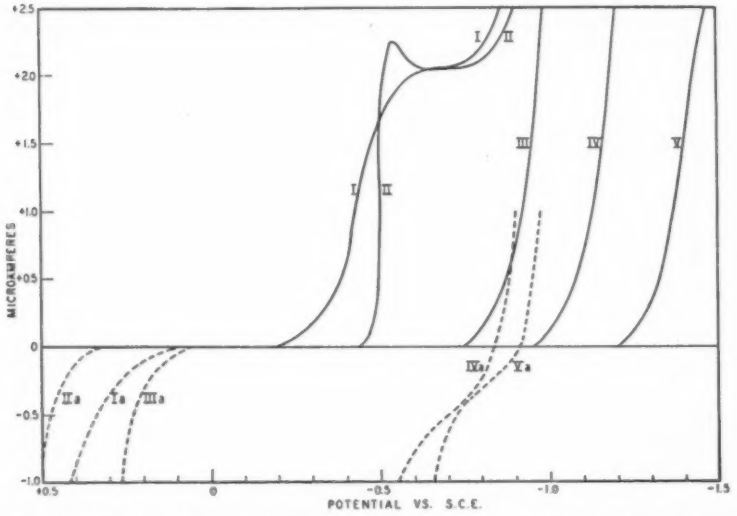

FIG. 4. Polarograms of millimolar palladium complexes obtained with a stationary platinum electrode using automatic recording. I, 0.3 M KCNS; II, 0.1 M NH_4OH; III, 0.1 M $Na_2S_2O_3$; IV, 0.1 M NaCN; V, 0.1 M NaCN + 1.0 M NaOH. The "a" curves are the corresponding dissolution waves.

the watch glass was covered with thin cellophane (3 mg./cm.^{2}) and mounted in the center of a $2\frac{1}{2}$ in. x $3\frac{1}{2}$ in. aluminum sheet having a hole in the center which was slightly larger than the watch glass. The electrodes were mounted in the same manner. All counts were corrected for decay, coincidence, size of aliquot, and counter geometry. All samples that were counted on platinum were corrected for the difference in back-scattering between platinum and glass.

RESULTS

Polarography

Information about the polarographic behavior of silver is rather limited. Because silver is more noble than mercury, solutions of silver react spontaneously with mercury producing waves of the type shown in Fig. 2.

Laitinen and Kolthoff (10) illustrated the general applicability of a solid polarographic electrode by using a solution of silver nitrate, but polarographic information about the complexes employed in the present investigation has not been reported. The curves shown in solid lines in Fig. 3 are exact reproductions of silver waves obtained with a platinum electrode using automatic recording.

The polarographic behavior of palladium at a dropping mercury electrode has been reported by another investigator (22) so Fig. 4 contains only the curves for reactions at a platinum electrode. Reduction waves were not found in cyanide and thiosulfate media where reduction of palladium was preceded by hydrogen evolution.

Deposition

Studies of rates.—The difference between the half-wave potentials for two reactions in a given solution is a crude measure of the degree of success

TABLE I. *Relative amounts of certain silver and palladium isotopes following a neutron bombardment of natural palladium*

Ratio	End of bombardment	4 hours after bombardment	8 hours after bombardment
$\frac{\text{Total Pd}}{\text{Pd}^{109}}$	7.0×10^6	8.6×10^6	1.1×10^7
$\frac{\text{Ag}^{109}\text{ (stable)}}{\text{Ag}^{111}}$	56	61	65
$\frac{\text{Pd}^{109}}{\text{Ag}^{111}}$	22	18	15
$\frac{\text{Total Pd}}{\text{Ag}^{111}}$	1.5×10^6	1.6×10^6	1.6×10^6

that one might expect in attempting to make a separation, regardless of whether or not both reactions are reversible. If both reactions are reversible, an exact calculation of the separation at any potential should be possible. If either one or both of the reactions are not reversible, the separation must be determined experimentally. As shown by the dotted lines in Fig. 3, all of the silver reactions are reversible.

A similar study on palladium is recorded in Fig. 4, and it shows that the dissolution wave is displaced at least +0.2 v. from the reduction wave in each case. For this reason it was not possible to make exact calculations for the separations on the basis of polarographic data; hence actual depositions were needed to determine the separability of the elements. Since both the percentage of the silver recovered and the degree of separation might change with the time of the electrolysis, rates of deposition were studied briefly.

The deposition rates for silver and palladium were determined under constant conditions of stirring, electrode size and shape, and volume of solution. A 20 ml. portion of an active solution, either silver or palladium, was electrolyzed in a cell of the type shown in Fig. 1. At various intervals

of time, a 0.100 ml. aliquot was pipetted from the cell, evaporated on a watch glass, and counted. As shown in Fig. 5, the relative rate of deposi-

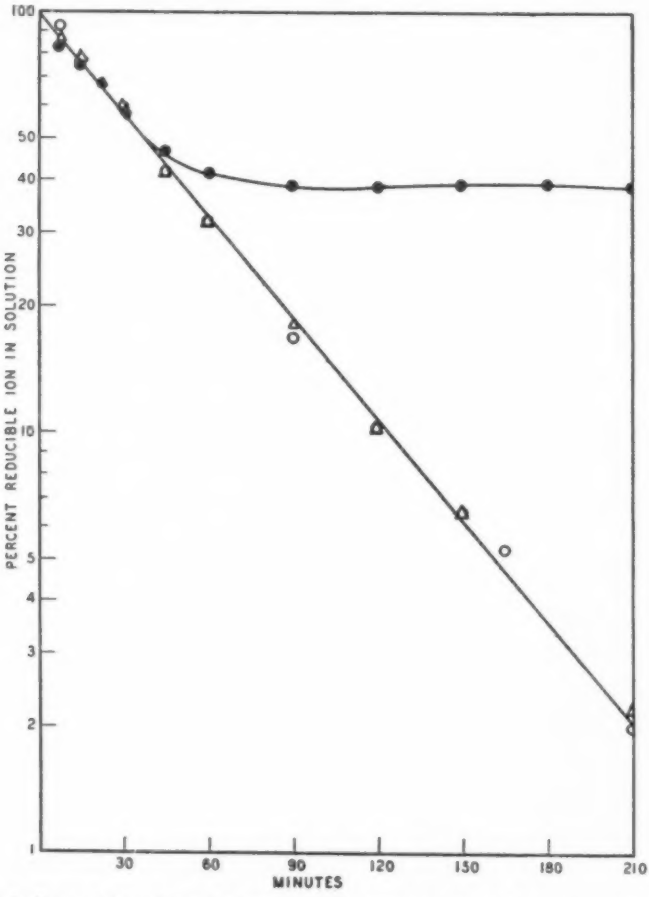

FIG. 5. Rate of deposition of silver and palladium at potentials more negative than the polarographic wave. ○—"carrier-free" silver in 0.1 M NaCN + 1.0 M NaOH electrolyzed at −1.200 v. vs. S.C.E., △—10^{-5} M silver in 0.1 M NaCN + 1.0 M NaOH electrolyzed at −1.100 v. vs. S.C.E., ●—10^{-3} M palladium in 0.3 M KCNS electrolyzed at −0.900 v. vs. S.C.E.

tion, at potentials more negative than the polarographic wave, was independent of the ion and its initial concentration. Palladium deviated noticeably toward the end of the electrolysis only because deposition was not complete under the conditions employed for the experiment.

A comparison of the half-wave potentials for silver and palladium in a given medium revealed that the reduction wave for silver always preceded that for palladium (see Table II). Since, in making a separation, one would work at potentials more positive than the palladium reduction wave (but more negative than the palladium dissolution wave), a knowledge of the rate of palladium deposition in this "irreversible" region was desirable.

Fig. 6 shows the data for cyanide and thiocyanate solutions. The data for cyanide were reproducible and indicated that equilibrium was attained in three hours; the data for thiocyanate were too scattered to allow a reliable curve to be drawn, and they did not indicate that equilibrium was being approached. In both cases, the percentage of palladium deposited, though small, represented an amount which was very large when compared to the total amount of silver in the original solution.

These experiments illustrate the usefulness of a polarograph in making rough estimates of the relative rates of deposition where an irreversible reaction is concerned. It is important to remember that changes in the concentration of either element will change the separation of the polaro-

TABLE II. *Half-wave potentials of millimolar palladium and silver solutions obtained with stationary electrodes using automatic recording*

Background solution	$E_{1/2}$ vs. S.C.E. in volts	
	Silver	Palladium
0.1 M NH_4OH	−0.02	−0.50
0.3 M KCNS	−0.22	−0.43
0.1 M $Na_2S_2O_3$	−0.41	—*
0.1 M NaCN	−0.84†	—*
0.1 M NaOH and 1.0 M NaOH	−0.79†	—*

* Hydrogen evolution preceded the palladium reduction wave.

† Exact value depends on rate of polarization.

graphic waves (and the deposition potentials) with a consequent change in the separability of the elements.

Studies of separations.—It was necessary to determine the separability of silver and palladium by carrying out deposition experiments because of the irreversible behavior of palladium and because of the absence of polarographic reduction waves for palladium in two complexing agents. Furthermore, insufficient information was available to allow one to predict with certainty the deposition behavior of traces. For that reason, it was necessary to study the electrolysis of silver experimentally. Although the resulting data should only apply strictly to the specific concentrations that were studied, moderate changes in the silver concentration have been found not to affect the results noticeably.

Electrolyses were carried out on 20 ml. portions of millimolar palladium solution, the palladium having previously been irradiated in the pile. Potentials were selected which were at least 0.1 v. more positive than the palladium polarographic half-wave potentials and, at the same time, sufficiently negative to deposit some silver. In all of the studies, the initial concentrations of silver and of palladium, the rate of stirring, and the time of electrolysis (30 min.) were held constant.

The degree of separation was calculated in terms of a separation factor which was arbitrarily defined as the fraction of the silver deposited divided

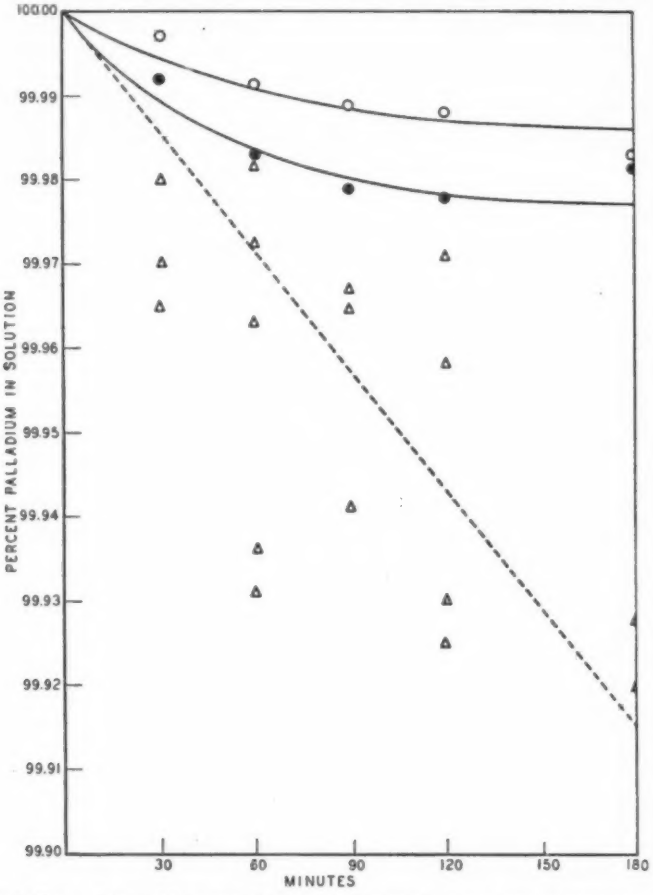

FIG. 6. Rate of deposition of palladium at potentials more positive than the polarographic reduction wave. ○—10^{-5} M palladium in 0.1 M NaCN + 1.0 M NaOH electrolyzed at −1.200 v. vs. S.C.E., ●—10^{-3} M palladium in 0.1 M NaCN + 1.0 M NaOH electrolyzed at −1.200 v. vs. S.C.E., △—10^{-3} M palladium in 0.3 M KCNS electrolyzed at −0.100 v. vs. S.C.E.

by the fraction of the palladium deposited. The fractions of silver and palladium deposited were derived by determining the original activity of each element by methods already described, and by determining the activities of each element in the deposit from decay curves similar to those in Fig. 7.

The separation factors and the supporting data for several solutions are collected in Table III. Most of these factors could be duplicated within

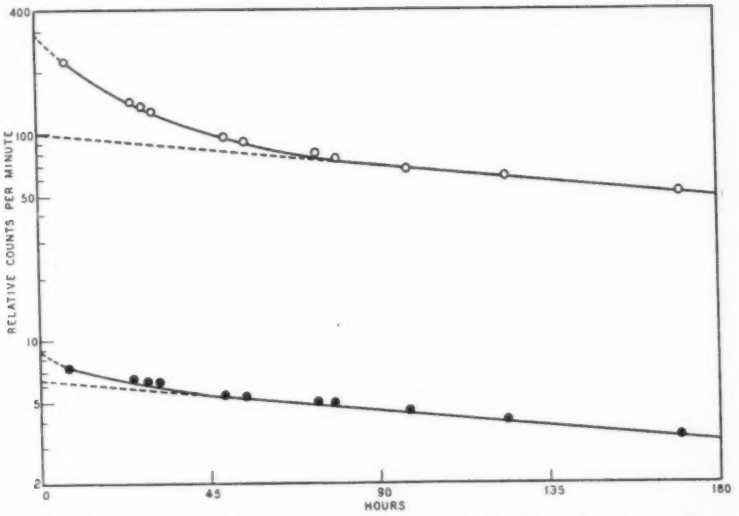

FIG. 7. Decay curves for attempted purification of silver by selective dissolution of silver in 0.3 M potassium thiocyanate. ○—electrolyte, ●—cathode after electrolysis.

TABLE III. *Separation of "carrier-free" silver from 10^{-3} M palladium using various complexing agents*

Supporting electrolyte	Cathode potential vs. S.C.E.	% Palladium plated	% Silver plated	Separation factor × 10^{-3}
0.1 M $Na_2S_2O_3$	−0.250	0.016	4.3	2.7
	−0.410	0.018	12	6.7
	−0.500	0.086	22	2.6
0.1 M NH_4OH	+0.150	0.008	8.4	10
	−0.015	0.017	21	12
	−0.350	0.14	47	3.4
0.3 M KCNS	−0.100	0.069	16	2.3
	−0.220	0.15	27	1.8
	−0.350	0.80	44	0.55
0.1 M NaCN	−0.805	0.008	0.35	0.4
1.0 M NaOH				
	−0.860	0.004	0.33	0.8
	−0.950	0.008	0.40	0.5
	−1.025	0.005	1.7	3.4
	−1.210	0.006	25	42

25 per cent. One should observe that the separations obtained in a cyanide solution are favorable primarily because of the small amount of palladium deposited. The amount of palladium plated from solutions other than

cyanide varied appreciably with a change of 0.4 v. in the applied potential whereas the amount plated from cyanide did not. At the same time, the amount of deposited silver also changed and, with the cyanide solutions, this change was particularly advantageous. Although it is not shown in Table III, the behavior and the results for cyanide solutions containing no sodium hydroxide were the same as for the solutions containing both hydroxide and cyanide.

Application of repeated electrolyses.—It is evident that selective dissolution of one element in a deposit or complete dissolution of a deposit in a fresh electrolyte followed by a second electrolysis should result in a corresponding increase in purity of the deposit. Three different approaches to this problem were examined: selective dissolution of silver, selective dissolution of palladium, and complete dissolution of the deposit followed by another electrolysis.

The first procedure was expected to present the problem of apparent insolubility of the silver as a result of its being buried almost completely in the palladium which would be present in great excess. Actually, the difficulty turned out to be quite different in that most of the palladium stripped from the electrode along with the silver in a short period of time. This is shown by Fig. 7 which contains decay curves of a thiocyanate electrolyte and of a deposit after about one hour of electrolysis at a potential of -0.075 v. vs. S.C.E. It was evident that dissolution of palladium was comparatively rapid even in the irreversible region of potential.

The second experiment in selective solution involved the use of cyanide to dissolve palladium from an electrode which was maintained at a potential sufficiently negative to deposit silver completely and hence, presumably, to retain it. Probably because the palladium was present in great excess, and therefore was able to "carry" silver (or disengage it) from the electrode, the cyanide removed the bulk of the activity from the electrode almost immediately. As a result, no enrichment of the deposit could be measured.

Because the above experiments on selective solution indicated that the deposit was removed almost completely in a very short time upon being exposed to a fresh solution of complex-forming electrolyte, it appeared that one would always be faced with the necessity of making a second complete electrolysis in order to effect an appreciable increase in the purity of the silver as well as to effect a better (preferably complete) recovery of the silver. Experiments using cyanide to strip the activity completely off the cathode followed by a period of electrolysis sufficiently long to recover most of the silver are shown in Fig. 8. Palladium activity could not be detected in the deposit recovered from the second electrolysis, whereas the activity remaining in the solution after the second electrolysis was primarily palladium. From the decay curves it was possible to calculate that the separation factor for each electrolysis was approximately the same, i.e., about 10^3. Assuming that the solution was initially 10^{-7} M silver and 10^{-3} M palladium, the second deposit contained about 1 per cent palladium. A third electrolysis should produce a correspondingly purer deposit of silver.

Some values for the overall recovery of silver from double electrolyses were 79, 78, and 76 per cent which in turn represented 85, 86, and 85 per

cent respectively of the recoveries permitted by the lengths of time employed for the electrolyses. It is not unlikely that these recoveries could be improved by modifying the procedure: the emphasis of these studies was placed on examining the purity of the deposit rather than on obtaining complete recovery of the silver.

DISCUSSION

Electrolytic procedure

Whenever a complex-forming electrolyte was displaced from the cell by distilled water at the conclusion of an electrolysis, serious loss of activity

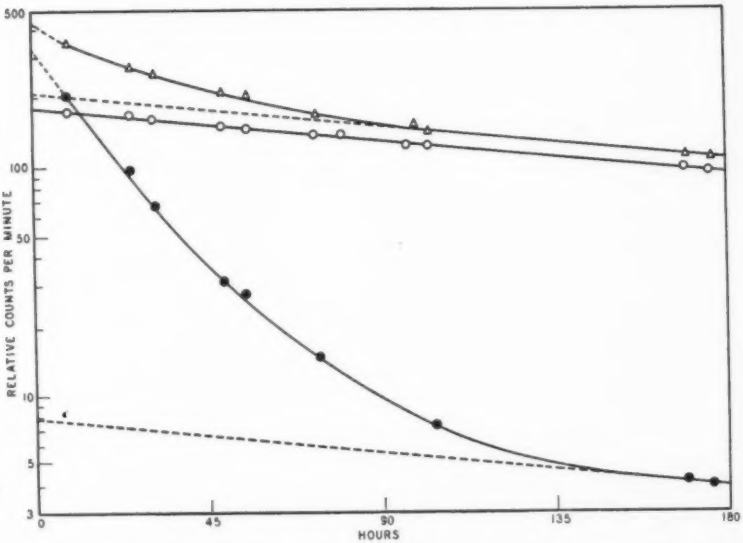

FIG. 8. Decay curves for two successive electrolyses in 0.1 M sodium cyanide plus 1.0 M sodium hydroxide. △—deposit after first electrolysis, ○—deposit after second electrolysis, ●—electrolyte after second electrolysis.

from the deposit always resulted, even though care was taken to make certain that electrical contact was not broken. For example, after one experiment in which pure silver activity was deposited from cyanide solution, 0.2 per cent of the original activity remained in the solution at the completion of electrolysis. After washing the cell with water, however, the wash liquid contained 17 per cent of the activity and only 81 per cent was found later on the cathode. Repetition of this experiment always gave similar results. Part of the difficulty appeared to be that the regulator could not maintain the proper potential on the electrode when the resistance of the solution changed rapidly. For that reason, solutions of electrolytes were substituted for the distilled water.

Attempts to flush cyanide solution from a cell by using a fresh portion of cyanide solution also resulted in a serious loss of silver activity from a deposit containing substantial amounts of palladium. On the other hand, the use of an electrolyte, such as sodium nitrate or sodium perchlorate, with which neither silver nor palladium formed stable complexes and hence toward which both elements were electrochemically more "noble," gave satisfactory results. One representative set of values for silver activity was: solution after electrolysis, <0.1 per cent; solution after washing cell, 0.4 per cent; activity found on cathode, 97 per cent.

During the course of this study, several observations were made concerning losses from sorption which may be helpful in devising procedures for

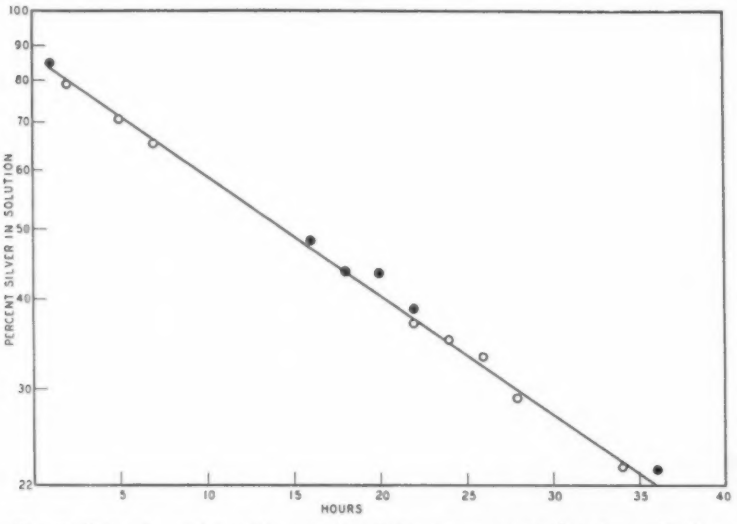

FIG. 9. Rate of sorption of "carrier-free" silver tracer onto glass from nitrate and perchlorate solutions of pH 4. ○—"carrier-free" silver in 0.1 M $NaClO_4$, ●—"carrier-free" silver in 0.1 M KNO_3.

other elements. For example, little difficulty was experienced with sorption on glass or agar surfaces when dealing with the very stable cyanide complex. Interference became noticeable, but not important, for solutions containing the ammonia complex of silver. On the other hand, serious losses from sorption, which took place primarily on the glass surfaces, always occurred when working with solutions of nitrate and perchlorate. The rate of loss due to this factor was reproducible. Fig. 9 indicates that an appreciable amount (about 15%) was very rapidly sorbed. By coating all of the glass surfaces with ceresine wax, the sorption losses for a five hour electrolysis of a nitrate solution were usually decreased to less than 5 per cent (9, 21). Some activity is sorbed on the scotch tape gasket from solutions of weak complexes, but the use of writing paper coated with ceresine wax will reduce this source of loss to a negligible value (9).

Radiochemical considerations

It is readily apparent from the experiments described in the present paper that the authors were concerned only with relative measurements. No attempt was made to determine the absolute number of counts or disintegrations in a sample except in making the rough checks of the yields of Pd^{109} and Ag^{111}. The need for absolute values of self-scattering and back-scattering were eliminated by reducing all measurements to a single set of conditions.

It was necessary to determine the relative amounts of back-scattering on platinum and on glass because most radiochemical analyses of solutions were made by evaporating an aliquot on a watch glass whereas most of the electrolytic deposits were counted on the platinum cathode. A glass-to-platinum ratio of 0.74 was found to be very reproducible.

There appeared to be a need for considering self-scattering because the activity of a solution before an electrolysis was determined by evaporating and counting a portion containing several milligrams of solid material, whereas the activity on a cathode was usually measured with less than 0.1

TABLE IV. *Per cent silver on cathode determined by two different methods*

Electrode	Per cent silver on cathode	
	By count of cathode	By count of strip solution
1	96	98
2	86	89
3	88	95
4	75	80
5	66	74
6	32	37

mg. of solid present. Experiments showed that a maximum error of about 5 per cent might be introduced from this source so this factor was ignored.

During the course of some experiments not reported in the present study, it was noted that the material balance for a particular electrolysis was often better than 95 per cent, but many times it fell between 90 and 95 per cent, and sometimes as low as 85 per cent. In no case was a significant amount of activity found in the wash solution, the agar bridges, or on the glass surfaces. The low recoveries appeared, therefore, to be the result of an unequal distribution of activity on the electrode, and radioautographs proved this to be so. The data in Table IV illustrate the extent to which the errors arising from the geometry of the deposit (as well as errors arising from differences in self-scattering) were decreased by dissolving the deposit in a solution containing approximately the same weight-percentage of solid (and often the same salts) as the original solution. After introducing this additional step, the material balances were almost always better than 96 per cent, and were often above 98 per cent. The latter figure was considered to be within the experimental limit of error of complete recovery for counting procedures of this type.

Errors arising from variations in the geometry of the deposit probably could have been avoided by using a different type counter and/or a smaller cathode. However, the counter employed for this study had the advan-

tage of being a widely used design. The alternative of using a smaller cathode was avoided because it would have necessitated longer periods of electrolysis as the result of a slower rate of plating. Such a change would have been unfavorable in working with the relatively short halflife of Pd^{109}.

CONCLUSIONS

It has been shown that polarograms obtained with a solid electrode provide a practical basis for judging the feasibility of a separation whether or not the reaction is thermodynamically reversible. After a deposition had been completed, a satisfactory recovery was made by the use of a wash liquid containing an electrolyte toward which the deposit was relatively "noble." The precision and the accuracy of the results was improved by dissolution of the deposit and estimation of the activity in the resulting solution.

Of the solutions tested, cyanide produced the best separation. By repeating the electrolysis, correspondingly purer silver was produced. Although the experimental data can only be applied strictly to solutions having the same concentration of silver, the information is sufficiently general to be useful for a comparatively wide range of trace concentrations.

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Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

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ELECTROLYTIC REFINING OF ANTIMONY BULLION[1]

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ABSTRACT

Antimony bullion of several compositons was electrolytically refined in electrolyte composed of antimony trifluoride and sulfuric acid at current densities up to 20 amp./ft.^{2} (2.2 amp./dm.^{2}). The effects of electrolyte circulation and of variation in the antimony content of the electrolyte were studied. The cathode-current efficiency was about 99%, and the deposits stripped well. Most of the copper, arsenic, and bismuth in the bullion went into the refined metal, and when the bullion contained sulfur and arsenic more than 99% of the gold and silver was recovered in the slimes. When the electrolyte contained insufficient antimony, the deposits were rough and loose. Copper and silver can be kept out of the refined metal by circulating the electrolyte through a cementation tank containing finely divided antimony.

INTRODUCTION

Koster and Royer (1) studied several methods for the electrolytic refining of antimony bullion obtained by smelting gold- and silver-bearing ore from the Yellow Pine mine at Stibnite, Idaho, and decided that, of the various electrolytes studied, the antimony fluoride-sulfuric acid solution was the most satisfactory. This electrolyte is essentially the same as that patented earlier by Roscher (2). Working with bullions that contained 80 to 60 per cent antimony, 9 to 25 per cent iron, 1 to 5 per cent sulfur, 10 per cent arsenic, and 8 ounces of gold and 15 ounces of silver per ton, at a current density of 6 amp./ft.^{2} (0.65 amp./dm.^{2}), and using an electrolyte containing 80 g./l. antimony and 500 g./l. sulfuric acid, Koster and Royer obtained antimony deposits that contained 60 per cent of the arsenic and only a few per cent of the sulfur and iron in the bullion. Current efficiencies were approximately 99 per cent, and virtually all of the precious metals were recovered in the slimes.

The purpose of the present investigation was to make a more thorough study of the electrolytic refining of gold- and silver-bearing antimony bullion from an antimony fluoride-sulfuric acid electrolyte. The samples of bullion used in this work were prepared in pilot-plant smelting tests by the Bradley Mining Company, Stibnite, Idaho, in cooperation with the Bunker Hill smelter, Kellogg, Idaho, from concentrates of gold- and silver-bearing antimony ore from the Yellow Pine mine at Stibnite. The analyses of the samples are given in Table I. The first three contained appreciable amounts of arsenic and sulfur, whereas the fourth contained virtually none. The copper in the samples is reported to have come not from the ore, which has a very low copper content, but from contaminated furnace linings. It

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is to be noted that the samples were much higher in antimony and silver and much lower in iron, sulfur, and arsenic than those used by Koster and Royer.

The experiments were carried out in a lead-lined cell that contained three anodes of antimony bullion, two cathodes of 18-gauge copper sheet, and 11.1 liters of electrolyte. Each anode weighed about 4.5 lb. (2 kg.) and was 7 in. (17.8 cm.) long, 4 in. (10 cm.) wide, and 0.69 in. (1.75 cm.) thick; the submerged portion was 5.25 in. (13.4 cm.) long and was drilled with eight 0.375 in. (0.95 cm.) round sample holes. The submerged cathode surfaces were 5.5 in. (14 cm.) long and 4.5 in. (11.4 cm.) wide, the total plating surface in the cell being 0.7 ft.^{2} (6.5 dm.^{2}). With fresh anodes the distance between anode and cathode faces was 1.1 in. (2.8 cm.). All connections exposed to cell spray were covered with DeKhotinsky cement to prevent corrosion. The cell was equipped with a liquid-level indicator and cooling-water tubes. A copper coulometer and an ammeter were used to measure current, and storage batteries were used for power.

All electrolyte was prepared from distilled water and C.P. antimony trioxide, hydrofluoric acid, and sulfuric acid. Before the cathodes were

TABLE I. *Average analyses of bullion samples*

Sample No.	Analysis (gold and silver in ounces per ton, other elements in per cent)										
	Au	Ag	Cu	As	Pb	Fe	S	Bi	Ni	Zn	Sb (by difference)
1	8.72	158.4	2.42	1.51	0.69	0.3	0.2	<0.001	0.02	0.01	94.3
2	1.11	51.7	.1	.85	.38	.02	.1	<.001	—	—	98.4
3	6.57	116.4	1.51	1.39	.48	.02	.73	.16	.02	<.01	95.3
4	3.22	148.6	2.03	<.02	.90	.06	.01	.28	.02	<.01	96.2

placed in the cell, they were washed with carbon tetrachloride and polished with No. 1 metallographic paper. The cathodes were replaced at various time intervals, ranging from 1 to 5 days. At regular intervals during the refining, usually just before the cathodes were changed, samples of electrolyte were taken from a point opposite the center of one of the cathode surfaces facing the center anode, about 1.0 cm. from the cathode surface. These samples, usually 250 ml. in volume, were replaced with equal volumes of solution of the same composition as the initial cell solution. Water was added daily to make up evaporation losses, and the cell temperature was maintained at 27° to 30°C. Each run was generally made with a single set of conditions and was usually carried on continuously as long as any of the anodes were usable. The pieces of anode scrap above and below the solution lines were weighed separately. All current efficiencies, anode and cathode, were based on the average equivalent weight of the metals in the bullion and deposits, respectively.

BULLION CONTAINING SULFUR AND ARSENIC

Without circulation of electrolyte

A series of three runs was made at cathode current densities of 5.8, 14.7, and 19.7 amp./ft.^{2} (0.63, 1.59, and 2.12 amp./dm.^{2}) respectively, without

circulation or agitation of the electrolyte. Bullion sample 1 (Table I) was used in these experiments and was cast into anodes in a vertical carbon mold. Fresh electrolyte containing 84 g./l. antimony as antimony trifluoride and 530 g./l. sulfuric acid was placed in the cell at the beginning of the first run and used throughout the series, being replenished with antimony trifluoride and hydrofluoric acid after each run. Each run lasted 8.08 to 24.17 days, and the six deposits in each run had a total weight of 2,977 to 3,489 grams. Since the bullion, refined metal, slime, and electrolyte compositions and the distribution of the elements for the several current densities were essentially the same (except for the concentration of antimony in the electrolyte near the cathodes), the averages for the three runs are given in Table II.

At 5.8 amp./ft.^{2} (0.63 amp./dm.^{2}), the deposits had a crystalline texture and were bright and smooth; occasionally they had trees and were copper-

TABLE II. *Electrorefining of antimony bullion without circulation of electrolyte (82 g./l. antimony in electrolyte)*

	Au	Ag	Cu	As	Pb	Fe	S	Ni	Zn	Sb
Analysis (Au and Ag in ounces per ton, other elements in per cent or grams per liter)										
Bullion	8.72	158	2.42	1.51	0.69	0.3	0.2	0.02	0.01	94.3
Refined metal	.03	.5	2.00	1.31	<.01	.006	.02	—	—	96.6
Washed slimes	365	6200	18.6	4.05	28.8	2.56	9.88[a]	—	—	5.0
Equilibrium concentration in electrolyte										
Average for cell	—	—	.8	.7	—	1.6[b]	—	.2[b]	.02	82
Near cathodes	—	—	.3	.2	—	1.7	—	—	—	60–35
Distribution at equilibrium, per cent (based on elements in bullion)										
Refined metal	<1	<1	80	90	<1	2[c]	10	—	—	—
Washed slimes	99	99	20	10	99	20	90	—	—	—

[a] SO_4 content, 10.9%.
[b] After last deposit.
[c] Not at equilibrium.

colored at the edges. As the current density increased, the deposits became rougher and the trees and copper color became more frequent and pronounced. At 19.7 amp./ft.^{2} (2.12 amp./dm.^{2}), the lower portions of the deposits were relatively smooth, while the upper portions were rougher and had a little loose metal. At all current densities, the deposits were in satisfactory physical condition and, being brittle, could easily be stripped from the cathode sheets by flexing them. The cathode current efficiencies were about 99 per cent and were not affected by the current density or by the thickness of the deposits.

At the beginning of the series, the concentrations of copper and arsenic in the electrolyte near the cathodes increased, reaching equilibrium[2] before the end of the first deposit of the first run. After this, the concentrations of these elements in the electrolyte near the cathodes and in the cathode

[2] This is not true equilibrium but is really a steady state at which the quantity of impurity going into the electrolyte is the same as the quantity coming out.

deposits remained fairly constant (Table II). The concentration of zinc in the electrolyte reached equilibrium before the end of the first run of the series. The iron and nickel contents of the bullion were so small and their tendency to deposit on the cathodes so slight that equilibrium was never reached, the iron and nickel concentrations in the electrolyte continuing to increase throughout the series. Most of the iron and virtually all the nickel in the bullion entered the electrolyte. The percentage of iron in the deposits remained constant during the series in spite of the change in the iron concentration of the electrolyte. Although the electrolyte was not analyzed for gold, silver, sulfur, or lead, material balances indicated that there were no appreciable quantities of these elements in the electrolyte. The concentrations of antimony, copper, and arsenic in the electrolyte near the cathodes were lower than in the electrolyte as a whole (Table II). For antimony, the concentration difference increased with current density, the concentration near the cathodes being 35 g./l. at 19.7 amp./ft.^{2} (2.12 amp./dm.^{2}) and 60 g./l. at the lower current densities. Such variations in concentration were not detected for iron, fluorine, or sulfate.

As indicated in Table II, virtually all the gold, silver, and lead and most of the sulfur in the dissolved bullion were recovered in the slimes, which were equal in weight to about 2.5 per cent of the bullion weight and assayed more than 20 per cent in precious metals. The refined metal contained most of the copper and arsenic in the original bullion and small percentages of the iron and sulfur. It is evident that, in order to prevent the deposition of copper and arsenic with the refined metal, these elements must be removed from the electrolyte. Furthermore, their low equilibrium concentrations in the electrolyte indicate that a high degree of purification would be necessary. The data on iron, nickel, and zinc are, of course, incomplete. It seems likely, however, that large amounts of iron can accumulate in the electrolyte without affecting the purity of the deposits.

For each 1,000 grams of deposit made at any of the current densities, 23 grams of antimony, 24 grams of fluorine, and 3 grams of sulfate were removed from the electrolyte; these values are based upon electrolyte and washed-slime analyses. The depletion in antimony resulted chiefly from the fact that the deposits contained a higher percentage of antimony than the bullion, creating a deficit that was made up from the electrolyte. In these experiments the anode and cathode current efficiencies were approximately equal. A small quantity of antimony (about 1 gram per 1,000 grams of deposit) was also lost in the slimes. The sulfate probably went to the slimes as lead sulfate. Hydrofluoric acid fumes were sometimes detected, and the fluorine losses are believed to have resulted from vaporization.

In general, the voltage for each deposit started low, rose to a maximum, and fluctuated considerably. As the current density and the anode age increased, the initial voltage increased, and the time required to reach the maximum value decreased. The voltage range at each current density was as follows: 5.8 amp./ft.^{2} (0.63 amp./dm.^{2}), 0.23 to 0.58 volt; 14.7 amp./ft.^{2} (1.59 amp./dm.^{2}), 0.31 to 2.1 volts; 19.7 amp./ft.^{2} (2.12 amp./dm.^{2}), 0.40 to 2.3 volts. If the anodes were rubbed with a "policeman" or if the electrolyte was agitated vigorously, the voltage dropped temporarily to its initial value, indicating that the rise in voltage was due

to formation of a film at the anode surface. No evolution of gas was detectable at the electrodes.

The anode scrap, which in this report is defined as the percentage of the anode weight below the solution line that remained undissolved at the end of the run, averaged 24 per cent for the three runs. There was no appreciable variation with current density. Although the weight of the anodes above the solution line was 25 per cent of the total anode weight in the laboratory cell, it would be only a few per cent of the total weight in a full-size, commercial cell. For this reason, the "tops" were not included in the scrap. The upper part of the submerged anode corroded faster than the lower part, so that, as corrosion proceeded, the anode decreased steadily in both thickness and width from bottom to top. Finally, the anode corroded through at the solution line (Fig. 1). Since this occurred long before

FIG. 1. Anode scrap—without circulation of electrolyte; 24%

the anode was consumed, the scrap was relatively high. It is believed that the tendency for the anodes to become wedge-shaped as they corroded was caused by stratification in the electrolyte, the antimony concentration increasing with depth. The composition of the anode scrap was about the same as that of the original anode.

Since the cell used in these tests had three anodes and two cathodes, the center anode had a cathode surface on each side, while each end anode had a cathode surface on one side only. Yet the center anode corroded at the same rate as each end anode and gave the same amount of scrap. Moreover, the end anodes corroded as rapidly on the sides away from the cathode surfaces as on the sides near them, indicating that all the anode surfaces were equally active, so that the anode current density for the cell was 20 to 30 per cent lower than the cathode current density.

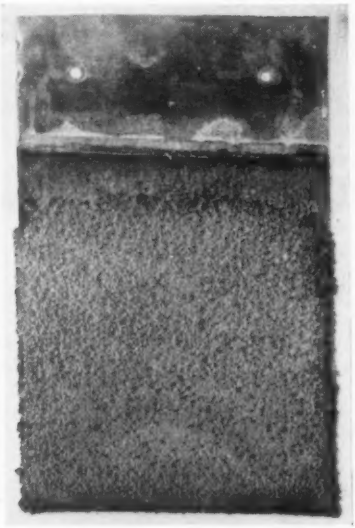

FIG. 2. Antimony deposit with sufficient Sb in electrolyte (c.c.d., 20 amp./ft.^{2})
FIG. 3. Antimony deposit with insufficient Sb in electrolyte (c.c.d., 20 amp./ft.^{2})

TABLE III. *Electrorefining of antimony bullion without circulation of electrolyte (103 g./l. antimony in electrolyte)*

	Au	Ag	Cu	As	Pb	Fe	S	Bi	Sb
Analysis (Au and Ag in ounces per ton, other elements in per cent or grams per liter)									
Bullion	6.63	118	1.47	1.40	0.48	0.02	0.73	0.16	95.3
Refined metal	.005	.3	1.12	1.34	<.02	.008	.02	.12	
Washed slimes	246	1555	20.8	.7	20.8	.12	25.3[a]	1.0	13.4
Equilibrium concentration in electrolyte									
Average for cell	—	—	.5	.6	—	.05[b]	—	.05	103
Near cathodes	—	—	.2	.2	—	.05	—	.05	55
Distribution at equilibrium, per cent (based on elements in bullion)									
Refined metal	0.1	0.3	80	98	<4	40[c]	3	80	—
Washed slimes	99.9	99.7	20	2	>96	15	97	20	—

[a] SO_4 content, 7.4%.
[b] After last deposit.
[c] Not at equilibrium.

Another series of runs, carried out at current densities of 5.7 and 13.5 amp./ft.^{2} (0.62 and 1.46 amp./dm.^{2}) with bullion sample 2 (Table I), gave similar results. During the run at 13.5 amp./ft.^{2} (1.46 amp./dm.^{2}), the average antimony content of the electrolyte in the cell dropped to 59 g./l. without ill effect on the deposits.

To study the effect of more concentrated electrolyte, a run was made at 20 amp./ft.^{2} (2.16 amp./dm.^{2}) with bullion sample 3 (Table I) and an electrolyte containing 103 g./l. antimony and 500 g./l. sulfuric acid. Five deposits with a combined weight of 2,491 grams were made in 112.79 hours at an average cathode current efficiency of 99.3 per cent. The deposits were all good; and, although the upper portions had a tendency to be rough, as previously encountered at this current density, there was no loose metal (Fig. 2). As shown in Table III, the build-up of impurities in the electrolyte, the impoverishment of the electrolyte near the cathodes, and the distribution of elements during refining were approximately the same as in the previous experiments. However, the iron and sulfur contents of the deposits were about the same as those shown in Table II, although bullion sample 3 contained much less iron and more sulfur than bullion sample 1. The anode current efficiency was again approximately the same as the cathode current efficiency, and 23 grams antimony, 13 grams fluorine, and 2 grams sulfate were removed from the electrolyte for each 1000 grams of deposits. The cell voltage was 0.35 to 2.8. The anode scrap was 44 per cent, and the pieces of scrap were wedge-shaped but less so than in previous tests (Fig. 4).

Circulation and composition of electrolyte

A series of runs during which the electrolyte was circulated at the rate of 35 ml./min. was carried out at a cathode current density of 20 amp./ft.^{2} (2.16 amp./dm.^{2}) with electrolyte of various compositions. The equipment and method used were the same as those previously described except for the addition of an air lift which raised electrolyte from a point near the bottom of one side of the cell to a 700 ml. tank from which it flowed by gravity to the solution surface on the other side of the cell. Bullion sample 3 (Table I) was used in these runs and was cast into anodes in a vertical steel mold.

The various electrolyte compositions, the concentrations of antimony in the electrolyte near the cathodes, the anode scrap, and the description of the deposits obtained in these experiments are given in Table IV.

The data show that when the antimony concentration of the electrolyte near the cathodes was 45 g./l. or more the deposits were all good, solid, coherent, and smooth. At 30 g./l. the upper portions of the deposits were rough and had some loose metal, and at 23 g./l. there was so much loose deposit that a considerable amount fell off the cathodes into the slimes (Fig. 3). In other experiments, in which the antimony concentration dropped to 12 g./l., all the deposit fell off the cathodes. These data and the information given previously show that loose deposits are caused by low antimony concentration in the electrolyte near the cathodes. By lowering the impoverishment of antimony in the electrolyte near the cathodes, circulation makes it possible to maintain the necessary concentration near the cathodes with a lower average concentration of antimony in the cell. For example, at 20 amp./ft.^{2} (2.16 amp./dm.^{2}), deposits made with circulated electrolyte having an average concentration of 51 g./l. antimony were better than those made with uncirculated electrolyte having an average concentration of 83 g./l.

The average cathode current efficiency for the first 5 runs (see Table IV)

was over 99 per cent, but in run 6 it dropped to 96.5 per cent. Loose metal that fell from the cathodes and was not weighed with the deposits accounted for only about one half of the drop in cathode current efficiency during run 6. Some gassing was detected at the cathodes. Although the anode current efficiency obtained with this bullion in an earlier run made without electrolyte circulation was 98.4 per cent, the average for these runs was only 96.6 per cent. The decreased anode current efficiency

TABLE IV. *Effect of electrolyte composition on deposits*

Run No.	Average composition of electrolyte, g./l.			Concentration of Sb in electrolyte near cathode, g./l.	Anode scrap, (%)	Deposit
	Sb	SO_4	F			
1	98	489	45	80	55	Solid, smooth
2	77	468	40	56	46	"
3	69	446	39	—	—	"
4	51	366	33	45	—	"
5	44	295	28	30	43	Somewhat rough, especially upper part; some loose deposit, especially upper part.
6	28	222	19	23	38	All deposits rough and loose, especially upper part.

FIG. 4. Anode scrap—without circulation of electrolyte; 44%

FIG. 5. Anode scrap with circulation

raised the electrolyte depletion to 42 grams antimony per 1000 grams of deposits; corresponding values for fluorine and sulfate remained 15 and 2, respectively. The cell voltages in these experiments usually started at 0.4 and rose to 2.9, and occasionally higher. This maximum voltage is considerably higher than the maximum of about 2.1 volts obtained with the other bullion samples studied and may be due to its appreciably higher sulfur content.

The anode scrap decreased as the electrolyte became more dilute. Circulation of electrolyte caused a change in anode corrosion, the tendency for the anodes to become wedge-shaped over their entire length being replaced by a tendency to become wedge-shaped only in a section about 1 in. (2.54 cm.) below the solution surface (Fig. 5).

The bullion, refined metal, and slime compositions and the distribution of the elements were essentially the same for all these runs and are summarized in Table V. Circulation caused a little more of the precious metals to enter the deposits, perhaps because it kept more of the slimes in suspension. But, as the data in Table V show, circulation had no appreciable effect on the distribution of the other elements.

The build-up of impurities in the electrolyte was the same for all the electrolyte compositions used. Circulation of electrolyte, in addition to decreasing the impoverishment of antimony in the electrolyte near the cathodes, eliminated the impoverishment of copper and arsenic; the copper and arsenic concentrations during these runs were approximately 0.3 g./l.

TABLE V. *Electrorefining of antimony bullion with circulation of electrolyte*

	Au	Ag	Cu	As	Pb	Fe	S	Bi	Sb
Analysis (Au and Ag in ounces per ton, other elements in per cent)									
Bullion	6.57	116	1.51	1.39	0.48	0.02	0.73	0.16	95.3
Refined metal	.09	1.41	1.19	1.33	<.01	.007	.02	.15	97.3
Washed slimes[a]	285	5068	14.5	.62	21.7	.09	29.7	.43	7.5[b]
Distribution at equilibrium, per cent (based on elements in bullion)									
Refined metal	1.5	1.2	77	99	<4	30[c]	3	94	—
Washed slimes	98.5	98.8	23	1	>96	5	97	6	—

[a] SO_4 content, 9.5%; F content, 0.1%.
[b] Without run 6 (Table IV) for which Sb content was 35%.
[c] Not at equilibrium.

Gold and silver analyses of these electrolytes, made for the first time in this investigation, showed that they contained as much as 0.07 mg./l. gold and 5 mg./l. silver.

ELECTROLYTIC REFINING OF ANTIMONY CONTAINING NO SULFUR OR ARSENIC

The refining of bullion without appreciable amounts of arsenic and sulfur (sample 4, Table I) resulted in marked differences in distribution of the precious metals and in anode corrosion. A run was made with this bullion sample at a current density of about 20 amp./ft.^{2} (2.16 amp./dm.^{2}) with circulation of electrolyte. The same equipment and experimental methods were used as in previous work, except that some of the depletion losses were made up by adding a concentrated solution of antimony trifluoride to the electrolyte at regular intervals. The high depletion of antimony made this necessary.

Over 4,900 grams of good, solid deposits were made at an average cathode current efficiency of 99.8 per cent and a cell voltage of 0.5 to 2.1. The deposition time for one of these deposits was 119.13 hours, and the deposit weighed 2,631 grams or more than 53 per cent of the combined anode

weights (submerged portions). This deposit was very rough, but there was no decrease in current efficiency. The data in Table VI show that about 4 per cent of the gold and 40 per cent of the silver went to the deposits. The first deposit had nearly the same precious metal content as the others, showing that equilibrium was quickly established. The percentage of copper going to the deposits also was increased over that for previous bullions. About 1.5 per cent of the silver in the bullion went to the electrolyte, and 5.5 per cent was unaccounted for; the silver unaccounted for may have been cemented out on the lead lining of the cell. Gold

TABLE VI. *Electrorefining of antimony bullion containing no sulfur or arsenic*
Cathode current density, 20 amp./ft.² (2.16 amp./dm.²)

	Au	Ag	Cu	As	Pb	Fe	S	Ni	Zn	Bi	Sb
Analysis (Au and Ag in ounces per ton, other elements in per cent or grams per liter)											
Bullion	3.25	149	2.05	<.02	0.88	0.05	0.01	0.02	<.01	0.28	96.2
Refined metal	.12	50.8	1.82	<.02	<.02	.01	<.01	—	—	.25	97.9
Washed slimes[a]	188	5145	.4	<.02	55.8	.03	—	—	—	.35	<.05
Equilibrium concentration in electrolyte											
Average for cell	0.03[b]	32[b]	.3	<.02	—	.3[b]	—	.07	<.01	.05	58–43
Near cathodes	—	9–27	.3	<.02	—	—	—	.05	<.01	.05	51–40
Distribution at equilibrium, per cent (based on elements in bullion)											
Refined metal	4	40	96	—	<2	24[c]	—	—	—	96	—
Washed slimes	96	60	4	—	>98	1	—	—	—	4	—

[a] Weight of washed slimes per unit weight of bullion, 0.016; SO_4 content, 8.2%.
[b] After last deposit.
[c] Not in equilibrium.

TABLE VII. *Distribution of gold and silver at lower current densities*

Cathode current density		Deposition time, hours	Weight of deposit, grams	Contents of deposits, oz./ton		Percentage of metals in bullion that entered deposits		Electrolyte content near cathodes, mg./l.	
amp./ft.²	amp./dm.²			Au	Ag	Au	Ag	Au	Ag
6.1	0.66	70.27	462	0.025	25.8	0.9	18.5	0.03	8.4
9.9	1.07	92.67	1017	.055	72.8	1.9	52.5	.03	35.4
15.3	1.65	48.00	795	.08	84.2	2.7	60.7	.03	45.9

[a] The washed slimes for the three deposits contained 98% of the gold and 46% of the silver in the bullion, and the final electrolyte contained 5% of the silver.

showed much less tendency to accumulate in the electrolyte than silver. The anodes neither formed wedge shapes nor corroded excessively at the solution lines and therefore were almost completely consumed. The run was discontinued when 0.7 per cent of the anodes remained. There was some evolution of gas at the anodes during this run. The average anode current efficiency for this run was 91.8 per cent and for two other runs, made with this bullion and stopped when 3 per cent and 50 per cent of the anodes remained undissolved, the values were 93.2 per cent and 95 per cent, respectively. The last few per cent of the anode metal probably corrodes

TABLE VIII. *Effect of adding sulfur or arsenic to bullion*

	Adding arsenic								Adding sulfur							
	Au	Ag	Cu	As	Pb	Fe	Bi	Sb	Au	Ag	Cu	Pb	Fe	S	Bi	Sb
Analysis (Au and Ag in oz./ton or mg./l. other elements in per cent or g./l.)																
Bullion	3.10	145	1.99	1.59	0.88	0.07	0.28	94.7	3.17	146	1.96	0.88	0.07	0.54	0.29	95.7
Refined metal[a]	.03	14.9	1.74	1.33	<.01	.01	.24	96.6	0.09	4.1	1.56	<.01	.004	.04	.26	98.1
Washed slimes[b]	160	6649	4.4	.72	45.	.08	.29	3.3	119	5364	8.4	31.	.13	28.	.21	3.0
Equilibrium concentration in electrolyte																
Average for cell	.03	3[c]	.6	.6	<.01	.2[c]	.1	61–54	<.03	.5[c]	.3	<.01	.4[c]	—	.1	59–45
Near cathodes	.03	3–19	.6	.6	<.01	.2	.1	55–50	.03	1–4	.4	<.01	.4	—	.05	52–44
Distribution at equilibrium, per cent (based on elements in bullion)																
Refined metal	1	11	94	92	0	15[d]	94	—	3	3	86	0	6[d]	10	97	—
Washed slimes	99	89	6	8	100	3	6	—	97	97	14	100	5	90	3	—

[a] Refined metal weights: arsenic run, 3,927 grams; sulfur run, 3,757 grams.
[b] Washed slimes contained 21% SO_4 in arsenic test and 28% SO_4 in sulfur test.
[c] After last deposit.
[d] Not at equilibrium.

at very low current efficiency. The electrolyte depletion for this experiment was 81 grams antimony and 19 grams fluorine per 1,000 grams of deposit, the high value for antimony being the result of the large difference between anode and cathode current efficiencies.

This bullion was also refined at current densities of 6.1, 9.9, and 15.3 amp./ft.^{2} (0.66, 1.07, and 1.65 amp./dm.^{2}) to study the effect of current density on the distribution of silver. The electrolyte contained 81 to 74 g./l. antimony, 360 g./l. sulfuric acid, 0.03 mg./l. gold and 5 to 48 mg./l. silver, and normal amounts of other impurities. The data in Table VII indicate that even at low current densities much of the silver was deposited with the refined metal.

Effect of adding sulfur and arsenic to bullion

Runs were made with portions of this bullion (sample 4, Table I) to which sulfur or arsenic had been added to determine if one of these elements would improve the recovery of silver. The electrolyte was circulated in the usual manner, and the current density was about 20 amp./ft.^{2} (2.16 amp./dm.^{2}). The initial electrolyte in each run contained about 60 grams antimony, 375 grams sulfuric acid, and 0.05 g./l. arsenic, traces of gold and silver, and various concentrations of other impurities. Data for these runs are summarized in Table VIII.

TABLE IX. *Effect of sulfur and arsenic in bullion on distribution of gold, silver, and copper*
(per cent based on elements in bullion)

	Gold		Silver		Copper	
	Washed slimes	Refined metal	Washed slimes	Refined metal	Washed slimes	Refined metal
Bullion sample containing sulfur and arsenic[a]	98.5	1.5	98.8	1.2	23	77
Bullion sample containing no sulfur or arsenic						
As received	96	4	60	40	4	96
Sulfur added	97	3	97	3	14	86
Arsenic added	99	1	89	11	6	94

[a] Data from Table V.

The average cathode current efficiency was 98.8 per cent, and all deposits were good, without loose material. Neither sulfur nor arsenic had much effect on the concentration of gold in the electrolyte; but, comparison of the data in Table VIII with those in Table VI shows that both elements lowered the concentration of silver, sulfur having much more effect than arsenic. In the arsenic run, 0.3 per cent of the silver in the dissolved bullion went to the electrolyte, while in the sulfur run the amount going to the electrolyte was insignificant. The effect of sulfur and arsenic on the distribution of gold, silver, and copper is summarized in Table IX. The increased percentages of these elements that go to the slimes as a result of the presence of sulfur or arsenic in the bullion is probably due to the formation of compounds insoluble in the electrolyte. The concentration of silver in the electrolyte fluctuated throughout both runs, but there was little variation in precious metal content among the deposits of each run.

Arsenic and sulfur both caused the end anodes to corrode less on the sides away from cathode surfaces than on sides next to them and to be consumed more slowly than the center anode. In the arsenic experiment the anodes did not become wedge-shaped but had a slight tendency to corrode faster at the solution lines. However, the center anode was 99 per cent consumed before it broke, and, although the experiment was discontinued at this point, the end anodes were still usable, although 75 per cent consumed. In the sulfur experiment the anodes became wedge-shaped to some degree in the region just below the solution lines, and all the anodes broke at the solution lines; scrap value for center anode was 1.5 per cent and for the end anodes 25 per cent. The anode current efficiencies were about 93 per cent, and the depletion of electrolyte was 84 grams antimony and 34 grams fluorine per 1000 grams of deposit. The cell voltages were: arsenic experiment, 0.35 to 2.1; sulfur experiment, 0.42 to 2.3.

Removal of silver and copper from electrolyte

Silver and copper can be precipitated readily from antimony electrolyte by cementation on metallic antimony. For example, when 250 ml. of electrolyte containing 0.039 g./l. silver and 0.39 g./l. copper were agitated in a paraffin vessel for 0.25 hour with 3 grams antimony bullion (minus 200-mesh) containing 51 oz./ton silver and 1.6% copper, the silver content of the electrolyte was lowered to less than 0.0001 g./l. and the copper content was lowered to 0.04 g./l. A series of tests was made with 250 ml. portions of electrolyte containing copper to determine the conditions under which the cementation reaction is rapid and complete enough for continuous use in conjunction with a refining cell. It is assumed that conditions sufficiently favorable for the precipitation of copper should be even better for the precipitation of silver, since the difference between the single electrode potentials (3) of antimony (0.2 v.) and silver (0.7995 v.) is much greater than the difference between the potentials of antimony and copper (0.3475 v.). The data, which are summarized in Table X, show that the precipitation of copper is rapid and nearly complete (tests 1, 8), that the reaction is still quite rapid when the copper content of the metal is up to 27 per cent, (test 2, 2a), and that cementation can be continued until the copper content of the metal is over 50 per cent (test 3). Pure antimony, refined metal, and bullion are equally effective. The weight of metallic antimony used with electrolyte of low copper content must be many times greater than the weight stoichiometrically equivalent to the dissolved copper if the reaction is to be completed in reasonable time, and with unsized metal increase in time is less effective than a proportional increase in amount of metal (tests 4–8). A portion of bullion (sample 4, Table I) was crushed to minus 200-mesh and split into "slimes" and "sands" by settling in water, the "sands" having 58 per cent of the original weight. Tests 9 to 14, carried out with these sized fractions, proved that cementation on relatively coarse metal is much slower than on finely divided metal.

To determine if the use of lead equipment will result in the loss of valuable metals, 250 ml. of electrolyte containing 3.1 g./l. copper was agitated for 10 hours with 5 grams test lead (minus 150-mesh). About 68 per cent of the copper was removed from solution, and the final metal contained 7.2 per cent copper, 5.4 per cent sulfate, 2.9 per cent antimony, and 78

per cent lead; 0.4 gram antimony was precipitated from the electrolyte for each gram of copper precipitated.

The information from the cementation tests was used in designing a short experiment to study the recovery of gold, silver, and copper from antimony bullion containing no sulfur or arsenic by circulating the electrolyte through a cementation tank during the operation of the cell. It was necessary to prevent the metal placed in the cementation tank from being distributed throughout the circuit as a result of the circulation. Equipment was made of lead and was arranged so that the electrolyte could be pumped from the bottom of one side of the cell to an elevated tank (650 ml.), from

TABLE X. *Cementation of copper on metallic antimony*

Test No.	Antimony metal				Agitation time, (minutes)	Copper in electrolyte[a]		
	Description	Weight, (gram)	Copper content, per cent			Grams per liter		Decrease, per cent
			Initial	Final		Initial	Final	
	Antimony metal, minus 200-mesh							
1	Pure	5	0.02	3.4	180	0.64	0.007	99
2	Refined	3	1.8	27.5[b]	180	2.8	—	—
2a	[c]	—	27.5[b]	27.8	5	.081	.049	40
3	Refined	3	1.8	52[b]	2,280	6.8	2.4	65
4	Bullion	0.3[d]	2.0	—	1	.087	.082	6
5	do	.3[d]	2.0	—	3	.087	.076	13
6	do	.3[d]	2.0	—	52	.087	.058	33
7	Refined	3.0	1.8	—	5	.087	.0033	96
8	Bullion	3.0	2.0	—	10	.087	.0015	98
	Antimony metal, "slimes" and "sands" from minus 200-mesh bullion							
9	Slimes	3.0	3.4	—	10	0.37	0.21	42
10	Sands	3.0	1.4	—	10	.37	.35	5
11	do	3.0	1.4	—	10	.11	.10	9
12	do	12.0	1.4	—	5	.11	.072	35
13	do	12.0	1.4	—	10	.11	.066	40
14	do	12.0	1.4	—	1,210	12.1	—	—

[a] Contained 60 to 80 grams antimony as antimony trifluoride and 300 to 475 g./l. sulfuric acid.
[b] Estimated.
[c] Used final metal from test 2, washed.
[d] Equivalent to 11 times the copper in solution.

which it flowed by gravity to the cementation tank (2,660 ml.), then to a cone-shaped settling tank (2,050 ml.), then to another settling tank (550 ml.), and finally to the opposite side of the cell (11.1 liters) at the surface of the electrolyte. The cementation tank was provided with a good agitator.

The initial electrolyte contained 61.4 g./l. antimony, 360 g./l. sulfuric acid, 0.005 g./l. copper, 0.06 g./l. arsenic, less than 0.03 mg./l. gold, 0.5 mg./l. silver, 0.15 g./l. iron, 0.035 g./l. nickel, and less than 0.01 g./l. zinc, bismuth, and lead. At the beginning of the experiment 200 grams of the "sands" previously described were placed in the cementation tank. The "slimes" would have been much more effective in the cementation process, but its use might have created a settling problem difficult to solve under

present experimental conditions. The electrolyte circulation rate was 220 ml./min., and every hour during the run 100 to 200 ml. of underflow from the settling tank was manually returned to the cementation tank. Every 12 hours the cathodes were replaced, and samples of electrolyte were taken at the settler overflow and from the cell.

The cell was operated for 47.65 hours at a cathode current density of about 20 amp./ft.^{2} (2.16 amp./dm.^{2}), and four deposits with a total weight of 995 grams were made at a cathode current efficiency of 99.4 per cent. The anode current efficiency was only 85 per cent and the depletion of antimony from the electrolyte was correspondingly large, 204 grams per 1000 grams of deposit. The deposits were all good and the cell voltage was normal. The concentrations of gold, silver, and copper in the electro-

TABLE XI. *Effect of cementation on electrolytic refining of bullion containing no sulfur or arsenic*

	Au	Ag	Cu	Pb	Fe	Bi	Sb
Analysis (Au and Ag in oz./ton or mg./l. (other elements in per cent or g./l.)							
Bullion[a]	3.35	157	2.1	1.0	0.049	0.29	95.96
Metal used in cementation tank[a]	2.24	126	1.4	.75	.032	.15	97.20
Refined metal	.08	11.5	.49	<.01	.019	.16	99.26
Cementation product	5.71	402.9	7.0	—	—	—	—
Washed slimes[b]	107.4	3439.9	2.4	42.6	—	—	17.7
Equilibrium concentration in electrolyte							
Average for cell	.03	<.5[c]	.11	<.01	.2[c]	.07	61–52
Near cathodes	.03	7–15	.17	—	.2	.07	53
Settling-tank overflow	—	<1	.10	—	—	—	—
Distribution at equilibrium, per cent[d] (based on elements in bullion)							
Refined metal	2	7	28	0			
Washed slimes	71	49	3	100			
Cementation product	19	34	59				

[a] Bullion sample 4, Table I.

[b] Weight of washed slimes per unit weight of bullion, 0.022; contained 17.4% SO_4.

[c] After last deposit.

[d] Accounted for only 92% of Au, 90% of Ag, 90% of Cu in material balance.

lyte and deposits came to equilibrium within 12 hours. Data on concentrations and distribution are given in Table XI. Only 2 per cent of the gold, 7 per cent of the silver, and 28 per cent of the copper in the bullion entered the deposits. Comparison of these results with those in Table VI shows that the cementation procedure markedly decreased the percentages of those metals entering the deposits. From 8 to 10 per cent of these metals was unaccounted for in the material balance and is believed to have been cemented out on the large lead surfaces or, being deposited in fine particles, to have adhered to the lead and not been recovered. The settling tank had an especially strong copper color at the end of the test.

In this experiment, the concentrations of silver and copper in the electrolyte near the cathodes were higher than those in the "whole cell" and those in the settler overflow. The percentages of silver and copper in the deposits probably could have been decreased merely by passing the electrolyte

back to the section of the cell between the cathodes instead of to one side of the cell. Furthermore, the presence of considerable copper in the settler overflow indicates that the cementation process can be improved. The use of finer cementation metal in higher concentrations, a larger cementation tank or several tanks in series, and manipulation of circulation rate are some of the possible ways to improve the process.

A material balance of the antimony bullion used as the cementation metal showed that, of the 200 grams added at the beginning of the experiment, 30 grams were unaccounted for. It is believed that this loss was due to dissolution of antimony in the circulating electrolyte, since the metal was finely divided and in contact with a large volume of electrolyte in rapid agitation.

The recovery of silver from the electrolyte by precipitation with hydrochloric acid and the removal of copper from the electrolyte by electrolysis at very low current density were briefly investigated and found to offer possibilities.

SUMMARY

1. Antimony bullion was refined electrolytically using an electrolyte containing antimony trifluoride and sulfuric acid at current densities as high as 20 amp./ft.^{2} (2.16 amp./dm.^{2}). The cathode current efficiency was about 99 per cent. The cell voltage started at about 0.4 and increased to 2 or 3 volts during the electrolysis.

2. Most of the arsenic, bismuth, and copper in the bullion went into the refined metal. When the bullion contained arsenic and sulfur, more than 99 per cent of the gold and silver were recovered in a high-grade slime. With sulfur- and arsenic-free bullion, however, a large part of the silver was deposited with the antimony. Sulfur was more effective than arsenic in keeping the silver out of the refined metal.

3. The deposits stripped well; and, if the electrolyte contained enough antimony, had excellent physical characteristics. At low antimony concentrations, however, the antimony tended to deposit in a loose form and to fall off the cathodes. Circulation of the electrolyte lowered the minimum concentration of antimony in the electrolyte at which good deposits could be obtained.

4. Data indicate that copper and silver can be kept out of the refined metal by circulating the electrolyte through a cementation tank containing finely divided antimony.

Any discussion of this paper will appear in the discussion section of Volume 95 of the TRANSACTIONS of the Society.

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